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(54) Title: FILTER MANUFACTURED BY MICROPYRECTIC SYNTHESIS

(57) Abstract

A modular filter for gases liquid and particulate matter is disclosed, the filter comprising at least two porous ceramic or ceramic modules. A regenerative filter is also disclosed comprising a means for filtering; and a means for regenerating said means for filtering said means for regenerating being integral with said filtering means. A method for coating articles with a conductive coating is also included. Devices which may be used in conjunction with both modular and/or regenerative filters are disclosed.

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FILTER MANUFACTURED BY MICROPYRECTIC SYNTHESIS

This application is a continuation-in-part application of PCT application serial number PCT/US95/04935 which is a continuation-in-part application of application serial number 08/395,576 which is a continuation-in-part application of application serial number 08/297,023 filed August 29, 1994, which is a divisional of application serial number 08/030,586 filed on March 12, 1993, now abandoned. This application is also a continuation-in-part application of application serial number 08/369,426 which is a continuation-in-part application of application serial number 08/353,727.

FIELD OF THE INVENTION

The present invention relates generally to filter devices for filtering gaseous, liquid and particulate matter. More specifically, the present invention relates to filter devices having a modulated design. Even more specifically, the present invention relates to the use of these devices in exhaust emissions aftertreatment systems. This invention also relates to a regenerative filter device comprising ceramic, metal-ceramic or inter-metallic composites. More specifically, the present invention relates to an integral heating element made in situ with a filtering device. The present invention also relates to a process for applying a conductive coating to a ceramic, ceramic composite or inter-metallic structure. The present invention further relates to peripheral and control devices used in conjunction with the filter devices.

BACKGROUND OF THE INVENTION

During the last few years, several studies have evaluated the health risks associated with exposure to engine exhaust emissions. As a result of these studies, several government and health organizations have decided to tighten the standards

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which apply to engine-run vehicles, their fuels and their particulate and gaseous emissions.

On November 15, 1990, the President of the United States signed into law the Clean Air Act Amendments of 1990. Beginning in 1994, the new law sets a performance criteria. Specifically, it requires buses operating more than 70 percent of the time in large urban areas (using any fuel) to cut particulates by 50 percent compared to conventional heavy duty vehicles. Also, beginning in 1994, the Environmental Protection Agency began requiring a yearly testing to determine whether buses subject to the standard are meeting the standard in use over their full useful life. Similar provisions exist in other countries and therefore a global effort is underway to find exhaust filters and cleaning devices which would help consumers and the industry in reacting to the stringent standards set by the law.

Because of the financial and logistical concerns with alternative fuels, transit authorities and bus engine manufacturers are seriously considering aftertreatment systems such as trap-oxidizer technology to meet 1993/94 EPA laws and regulations. Bus engines, for example, run on a stop-and-go cycle which forces the engines to operate with a dirty, sooty exhaust. Second, these vehicles operate in dense population areas and hence, bus exhaust and pollution is considered a greater health hazard than over-the-road trucks. Third, environmentalists would like to be as clean as possible even if it means going beyond EPA regulations. These and other factors make trap oxidizer technology very attractive, provided that its long-term durability

can be proven and provided it is made available at reasonable costs.

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The 1993/94 EPA law and regulations are only the first step in a series of ever-tightening regulations to follow. For the diesel engines industry, the next step in regulation occurs in 1998, when the laws require tighter NO_x control. Even though NO_x reduction for 1994 levels was achieved by improved engine design, it is generally accepted that to meet the 1998 levels of 4 g/Bhp-h NO_x, diesel engines will have to use aftertreatment systems. As the NO_x level is reduced, however, generally the particulate level increases. Hence, in trying to meet the 1998 low NO_x levels,

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engine manufacturers are faced with increased particulates, which require further use of aftertreatment devices such as converters and traps.

Aftertreatment devices of the present invention made of ceramic, ceramic composite or inter-metallic filter devices, as well as the heating elements (which may be the identical material as the ceramic, ceramic composite, or inter-metallic filter devices), provide improved converters and trap systems which offer the flexibility, efficiency, and cost-effectiveness needed to meet the challenges presented by present (1994) and medium-term (1998), diesel emissions regulations. Preferably a conductive coating may be applied to the filter devices of the present invention. This coating may act as a heating element. Also preferably, the filter devices may be micropyretically synthesized. "Micropyretics" or "micropyretically synthesized," as used herein refers to self propagating high temperature synthesis as discussed in the review article by Subrahmanyam et al., in The Journal of Macromolecular Science at Vol. 27, p.p. 6249 - 6273 (1992).

The filter devices used in aftertreatment trap systems are the core of the system and great efforts are being made to fine-tune the existing systems to improve their effectiveness and durability. One of the problems of the current technology is in "regenerating" the filter by burning off the accumulated particulate matter. Initiating and controlling the regeneration process to ensure reliable regeneration without damage to the trap is the central engineering problem of trap oxidizer development today. The reason is that over time, the filter becomes loaded with the soot it has trapped and must be cleaned or "regenerated". The process of regeneration burns or "oxidizes" the soot collected within the filter. The cleaned filter can be used many times provided it can be successfully regenerated many thousands of times over its lifetime without failure. Another problem faced by the current technology is the need for optimization of the filter structure, as in a modulated design. Yet another problem of the current technology is that currently available filter materials are not optimally thermally shock resistant nor are they highly thermally cyclable, as in micropyretically manufactured materials.

Presently, most of the available aftertreatment trap systems are based on the cellular cordierite ceramic monolith trap. These traps have not been efficient at collecting soot, or at collecting a large fraction of the particulate soluble organic fraction (SOF). Also, these traps have several other limitations and leave much room for improvement. For example, the straight channeled ("honey-comb") structure of the filters optimizes neither stream line distortion nor surface area, for particulate collection. Further, the cordierite ceramic used in today's filters is expensive.

An initial attempt at solving some of the above described problems in aftertreatment systems was provided by the ceramic fiber coil traps developed by Mann and Hummel and Daimler Benz in West Germany. These traps were composed of a number of individual filtering elements, each of which consisted of a number of thicknesses of silica fiber yarn wound on a punched metal support. A number of those filtering elements were suspended inside a large metal can to make up a trap. However, failures during German field demonstrations appear to have reduced or eliminated further work or application of this system, according to "Diesel Particulate Control Around the World," Michael P. Walsh et al. part of "Global Developments in Diesel Particulate Control" P-240, publ. SAE, Inc. (Feb. 1991).

Numerous other trapping media have also been tested or proposed, including ceramic foams, corrugated mullite fiber felts, and catalytic coated stainless steel wire mesh.

With respect to regeneration, many different concepts are being tested. They range from primitive off-board regeneration of the filter in an external oven to sophisticated on-board automatic electrical or burner regeneration systems using electronic controls and include catalytic injection systems. These approaches to regeneration can generally be divided into two groups: passive systems and active systems. Passive systems must attain the conditions required for regeneration during normal operation of the vehicle. Active systems, on the other hand, monitor the build up of particulate matter in the trap and trigger specific actions leading to regeneration when needed.

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Passive regeneration systems face special problems on heavy duty vehicles. Exhaust temperatures from heavy duty diesel engines are normally low, and recent developments such as charge air cooling and increased turbo charger efficiency are reducing them still further. Under some conditions, it would be possible for a truck driver to drive for many hours without exceeding the exhaust temperature (around 400-450°C) required to trigger regeneration. Active systems, on the other hand, are generally expensive, often requiring complex logic and electronics to initiate regeneration.

In addition to the problems of the presently available aftertreatment systems addressed above, the high concentration of soot per unit of volume in the cordierite makes these traps sensitive to "regeneration" conditions. Trap loading, temperature, and gas flow rates must be maintained within na fairly narrow window. Otherwise, the trap fails to "regenerate" fully, or cracks or melts to overheating because the high temperature gradients in the filter monolith damage the cordierite structure.

Engine and catalyst manufacturers have also experimented with many catalytic converters and with a wide variety of regenerative catalytic traps as solutions to the aftertreatment problems described above. Precious metal catalytic traps are effective in oxidizing gaseous hydrocarbons and CO as well as the particulate SOF but are relatively ineffective in preventing soot oxidation, a particular problem for diesel engines. Moreover, these metals also promote the oxidation of SO₂ to particulate sulfates such as sulfuric acid (H₂O₄). Base metal catalytic traps, in contrast, are effective in promoting soot oxidation, but have little effect on hydrocarbons, CO, NO or SO₂. Another disadvantage of precious metal catalysts is that they are very expensive.

Unlike a catalytic trap, a flowthrough catalytic converter does not collect most of the solid particulate matter, which simply passes through in the exhaust. The particulate control efficiency of the catalytic converter is, of course, much less than that of a trap. One of the major disadvantages of the catalytic converter is the same as with the precious metal catalytic particulate trap: sulfate emissions. The main

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object of the catalysts used is to raise the exhaust temperature to a point that could convert the gaseous compounds to safer gaseous emissions. The catalysts undergo chemical reactions which raise the temperature of the exhaust gases allowing them to be converted to the safer gases. One of the major reasons which catalytic material and treatments are used to assist in trap regeneration, is that none of the heating systems attempted, such as diesel fuel burners, electrical heaters and other heaters have been successful. However, if there were a regeneration system in which a converter or trap could be used without a catalyst for regeneration, the above-listed objects would be achieved.

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With respect to processes for the manufacture of porous ceramic articles, U.S. Pat. No. 3,090,094, issued May 21, 1963 to K. Schwartzwalder et al, discloses a method of making an open-cell porous ceramic article which comprises immersing an open-cell spongy material, preferably polyurethane, in a slurry containing a ceramic coating material to coat cell-defining walls of the spongy material, removing excess slurry from the spongy material, and firing the coated spongy material at a temperature and for a time sufficient to remove the spongy material and form a hardened, vitrified structure. The ceramic coating material may include particulate zirconia, zircon, petalite, mullite, talc, silica and alumina, having particle sizes ranging from - 80 mesh to - 600 mesh. A binder such as clay, sodium silicate, and calcium aluminate and phosphoric acid, is preferably present in the slurry. Firing is conducted at 500° to 3000° F. (260° to 1650° C.), preferably at 2100° to 2950° F. (1150° to 1620° C.).

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U.S. Pat. No. 3,097,930, issued Jul. 16, 1963 to I. J. Holland, discloses a method of making a porous shape of sintered refractory material which comprises impregnating a foamed plastic sponge shape with a suspension of refractory particles, drying the impregnated shape, and firing the dried shape in an inert atmosphere to volatilize the sponge material and to sinter the refractory particles. The impregnation and drying steps may be repeated. The foamed plastic sponge may be polystyrene, polyethylene, polyvinyl chloride, latex, or polyurethane, the latter being preferred. Refractory materials include clays, minerals, oxides, borides, carbides, silicides,

nitrides and mixtures thereof. Specific examples used alumina, beryllia and china. clay with particle sizes ranging from less than 1 to greater than 10 microns. Firing was conducted at 1700° C for alumina and 1350° C for china clay.

5 U.S. Pat. No. 4,697,632, issued Oct. 6, 1987 to N. G. Lirones, discloses a ceramic foam filter, insulating refractory lining, and a melting crucible, and a process for production thereof, which comprises providing an open-cell foam pattern, impregnating the pattern with a ceramic slurry, burning out the foam pattern at a temperature between 1400° and 2200° F (760° and 1205° C.) to form a ceramic substrate, impregnating the ceramic substrate with additional ceramic slurry, and 10 firing the impregnated ceramic substrate at a temperature of 2200° to 3400° F. (1205° to 1870° C.). The foam pattern material may be a flexible polyurethane, polyethylene, polypropylene or graphite. A suitable ceramic slurry contains from 1% to 20% silica (dry weight), and from 99% to 80% alumina (dry weight), with a viscosity between 5 and 20 seconds and a film weight between 1.0 and 8.0 grams per standard six inch square plate. Preferably the slurry includes a suspending agent, a wetting agent and a defoaming agent. Zirconia may also be used as ceramic material.

U.S. Pat. No. 3,111,396, issued Nov. 19, 1963 to B. B. Ball, discloses a 20 method of making a porous metallic article which comprises impregnating a porous organic structure with a suspension of powdered metal, metal alloy or metal compound, and binder, slowly drying the impregnated structure, heating at about 300°-500° F. (150°-260° C.) to char the organic structure, and then heating at about 1900' to about 3000' F. (1040' to 1650' C.) to sinter the powder into a porous 25 material.

Other United States patents relating to porous ceramic filters and methods for making them include: 3,893,917 - July 8, 1975 - M. J. Pryor et al; 3,947,363 -March 30, 1976 - M. J. Pryor et al; 3,962,081 - June 8, 1976 - J. C. Yarwood et al; 4,024,056 - May 17, 1977 - J. C. Yarwood et al; 4,081,371 - March 28, 1978 - J. 30 C. Yarwood et al; 4,257,810 - March 24, 1981 - T. Narumiya; 4,258,099 - March 24, 1981 - T. Narumiya; and 4,391,918 - July 5, 1983 - J. W. Brockmeyer.

None of the above patents disclose or suggest the desirability of using conductive ceramic, metal-ceramic or inter-metallic filters, which can also be used as heating elements. The problems associated with the prior art methods are similar to the problems associated with the method described in US Patent No. 5,279,737, which problems are described in greater detail below.

US Patent No. 5,279,737 ("the '737 patent") discloses a process for producing a porous ceramic, ceramic composite or metal-ceramic structure by micropyretic synthesis wherein a form polymer shape is impregnated with a slurry of ceramic precursors and ignited to initiate micropyretic synthesis, thereby attaining a ceramic, ceramic composite or metal-ceramic composite article having interconnected porosity. The '737 patent is incorporated by reference into the present application, in its entirety.

Nowhere does USP 5,279,737 disclose or suggest a modulated filter comprising at least two porous ceramic or ceramic composite modules. The importance of the modulated design lies in the fact that by having a modulated system one can introduce very thin slices of the ceramic filters with pore sizes of 20 to 30 pores per inch, which are more efficient for particle trapping than larger pore sizes, such as 10 pores per inch. Also, if a whole filter trap constituted a single filter unit that was 20 or 30 pores per inch, the pressure drop would be too great and the back pressure would cause engine failure. With the modulated design, however, it is possible to use these pores sizes and insert therein membranes or slices of the filter of different thicknesses to achieve desired results. Some slices can be very thin, but have a very low pore size, for example, 50 pores per inch. A second advantage of the modulated design is that in combination with the heating elements, it is much easier to keep the filters "clean" because smaller pores are generally easier to block and more difficult to clean. In sum, the modulated design allows for an infinite number of variations of the filters and its applications by varying the pore sizes and the thicknesses of the modules as well as the number of modules in the overall filter.

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As will be now be described, the coating process of the present invention also constitutes a novel and unobvious improvement over the process described in the '737 patent. The impregnation step in the '737 patent is achieved by dipping the polymeric foam in the slurry with which it is to be impregnated. This step is very cumbersome and awkward. Also during processing using the invention of the '737 patent, one has be extremely careful so that the "green structure" (the structure before sintering, micropyretic or otherwise), does not "collapse." Collapse as used herein refers to dissolution of the ceramic in structure, before sintering, before or after burning of the polymeric foam. The process of the '737 patent may also give rise to "distortion". Distortion as used herein means physical distortion which results from large structure sagging under its own weight prior to burning of the polymeric foam. impregnation of the present process is achieved by (a) fluidizing said slurry with steam and spraying the shape with said fluidized slurry or (b) heating said slurry so as to reduce its viscosity and spraying the shape with said reduced viscosity slurry. This method of impregnation eliminates the above listed problems. Additionally, the steam or hot liquid constituent of the spray better dissolves certain constituents, such as calcium carbonates and silicates (cements) such as (CaO)3.(SiO2)2.(H2O)3, which lead to a high green and final strength by precipitating out on the deposited surface as a cement. The present process also results in more uniform thickness of the ceramic.

In the past, it was extremely difficult to incorporate a heating device into a filter because thermal cycling problems from incompatible thermal expansions of the heating element and filter. This made it difficult to have a filter with an integral heating element. The material used for the heating elements are typically molybdenum disilicide based. This material is able to heat to 550°C in only a few seconds, which combats the well-known problem of cold-start emissions in motor vehicles. Other superior properties include high emissivity of approximately 0.9, as compared to other heating elements which have emissivities of 0.4 to 0.75. The fact that the heating element is integral with the filter provides the advantage of less complexity, less moving parts and less cost. Most other systems depend upon many complex systems including logic and electronics to heat the filter or the exhaust gases,

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which is very costly and problematic. All materials made by the micropyretic technique experience a large temperature gradient of more than 1000 centimeters per millimeter during manufacture. This includes both filters and heating elements made by micropyretic technique. Due to the extreme conditions that the materials must endure during synthesis, the materials made by the micropyretic technique result in porous ceramics which are extremely thermally shock resistant, highly thermally cyclable and forgiving when contacted with the heating element. Because they possess these qualities, they are extremely well-suited for exhaust aftertreatment systems.

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To date, such rapid heating elements were not available. Non micropyretic heating elements even though made principally of molybdenum disilicide or silicon carbide are extremely expensive. Furthermore, they cannot heat as rapidly because they are not manufactured by the micropyretic technique. Another reason why heating elements have not been used in situ with the types of filters most commonly used today, is that the extruded cellular configuration of the presently available filters is ill suited for integral heating elements. The extruded channels made of the ceramic act as an insulator with respect to the other channels. Therefore, one would need many heating elements, one per cellular channel to have an in situ heating configuration, a highly impractical and extremely expensive proposition.

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The in situ heating elements would also enhance the catalytic converters already in use, today. Catalytic converters are heated during operation, and the EPA specifies a minimum time in which the catalysis bed must reach operating temperature. The standard solution has been to add an "pup" converter -- a second, small converter upstream of the main unit. It acts like an igniter, and heats the exhaust stream rapidly, but little else about them is satisfactory. Even a small converter adds significant costs. It is often difficult to fit even a sizable converter into limited space, and it creates shielding problems by placing another source of intense heat close to engine components. All of these problems are overcome by the integral in situ heating elements of the present invention.

Several different methods have been attempted to heat catalytic converters, including miniature radio transmitters that activate a non contact heating device heater, and additional catalysis. The present invention solves the necessity of heating catalysts without the expense and complexity of the prior art.

There is also a great need for technological improvements in catalytic converters and other engine emission reduction devices because there is a finite limit to the amount of platinum the most commonly used catalyst. Moreover, platinum is extremely expensive.

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The idea of having an in situ heating element within a filter has many applications outside of exhaust systems, as well. One of these applications would be in a simple heating device. One of the major advantages is that the heating element is actually inserted into the filter rather than the heat being supplied from outside the filter.

With respect to the regenerative aspect of the present invention, US Patent No. 5,094,075, issued March 10, 1992 to Heinrich Berendes, discloses a particulate filter that can be regenerated by means of a burner working in the main engine exhaust stream. Regeneration is achieved by means of a burner to which fuel and oxygencontaining gas is supplied in a variable proportion. By this means, the burner produces the output required to achieve the regeneration temperature in the diesel engine. This patent requires an outside burner, instead of an in situ integral heating element, in order to regenerate the filter.

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US Patent No. 5,015,381, issued May 14, 1991 to M. Edmund Ellion, et al, discloses a fluid filter element, filter, and process for its fabrication, wherein the filter element includes a flat base and a thin layer deposited thereupon having a channels though which a fluid may flow. In operation, the element is pressed against a flat surface, preferably against the backside of another element and a stack of filter elements, wherein the channels become closed conduits. The channels have a minimum requirement of thickness of the layer so that larger particles may not pass

therethrough. Fabrication of the thin layer with the channels therein is preferably accomplished by masking a pattern corresponding to the channels and then vapor depositing the remainder of the thin layer, as masking and deposition permits actuated control of the heights of the deposited layer and then the minimum dimension of the channels. This patent does not disclose the modular design nor does it account for regeneration of soot and particulates.

US Patent No. 5,001,899, issued March 26, 1991 to Enrique Santiago, et al, discloses a method and apparatus for cleaning of a soot filter in the exhaust line of a diesel engine with a combustion chamber placed in front of the soot filter where fuel nozzle and adapted electrical ignition method is built and thereby enabling the afterburning of the exhaust without secondary air. The exhaust in the combustion-chamber is mixed with the fuel which is injected through the fuel nozzle, and ignited by an ignition device with the existing portion of the unburned oxygen. The half exhaust effects the burndown of the accumulated soot in the soot filter. The apparatus disclosed herein is complex and requires many parts and does not teach a simple integral heating element to burn the soot in the filter.

"Regeneration Performance Of A Catalyst Versus Non-Catalyst Ceramic Membrane Diesel Particulate Trap", Rich Helfrich, et al, Global Developments and Diesel Particulate Control P-240 Society of Automotive Engineers, Inc., 121-132 (February 1991), describes a ceramic foam trap system using a parallel flow stacked element design. The individual elements are bonded together to form subassembly of 12 to 14 elements. The ceramic foam filter elements are non-reticulated material with a microporous membrane on a down stream (outer) side of the filter element. The trap itself has a center inlet through which the exhaust flows in the individual elements by way of the annular inlet ports (formed by adjacent elements). The elements in this invention are all the same size and each have the same function. The filtration of the gas in such a system is in a 'parallel' fashion and such a filter system is clearly non-modulated as described and claimed herein.

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US Patent No. 4,400,352, issued August 23, 1983 to Ovea Rehnburg, et al, discloses a method and device for optimizing purification of diesel exhaust gases, the purification being carried out by a catalysis. This invention does not disclose modulated design nor does it disclose incorporating a heating element into the filter for regeneration.

"Gassing Truckers", The Economists Newspaper Limited, Business Finance and Science: Science and Technology: Pg. 97 describes a particle trap which works like filters in the exhaust pipe using two traps and switching between them, so one trap filters while the other one burns the collected particles. That article admits, that despite years of research, those traps were still unreliable, strongly indicating the need for reliable particle traps. Although the design described has two separate filter units, it does not teach the modular design of the present invention.

U.S. Patent No. 5,334,570 discloses a porous catalyst support which may be used in a catalytic converter for treating automotive exhaust gases. The desirability of increasing "open frontal area" available for filtration is recognized. However, no mention or suggestion is made of increasing roughness to achieve this objective.

SAE International No. 930129, entitled Production Experience of a Ceramic Wall Flow Electric Regeneration Diesel Particulate Trap by Kejetin et al., described a dual ceramic wall flow electric regeneration diesel particulate trap. No suggestion or disclosing of modulation, conductive coated filter or in-situ heating elements is provided. Also, the electrical heating system disclosed is before (downstream of) the filter system. No heating element integral with the filter is disclosed or suggested. Also much greater power is required for the ignition of the filter disclosed in this article as compared to the filters of the present invention.

SAE International No. 920140, entitled a Study on Regeneration of Diesel Particle Trapper by Electrical Self-Heating Type Filter describes silicon carbide based filters, which themselves can be heated. While no specific indication of the internal structure of the filter is given, the article states that the material is formed by

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extrusion. When extrusion is used as a means of manufacture of ceramics invariably straight walled products are provided. This appears to be borne out by Fig. 3 of the article. Also, 4 KW of energy is required for ignition of a SiC filter because of the extremely high resistivity of SiC (of the order of $10x10^6 \mu$ ohm-cm), as opposed to the relatively small energy required for ignition of the filter of the present invention. Modulation is not disclosed or suggested nor are filters coated with a conductive material.

Several United States patents assigned to Donaldson Company, Inc. disclose regenerative filters with separate (non in-situ) heating elements for regeneration purposes. See United States patents 4,878,928; 5,053,062 and 5,224,973.

For the foregoing reasons, there is a need for an aftertreatment system of high effectiveness, low complexity and low cost, as well as a regenerating system incorporating a heating element integral with an exhaust ceramic, metal-ceramic or inter-metallic composite filter or a conducting coating applied to the filter which then functions as a heating element wherein the filter materials are highly thermally cyclable.

20 SUMMARY OF THE INVENTION

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While not exclusive, the following describes some of the important features and objectives of the present invention.

An object of the present invention is to provide improved catalytic converters and filters using the ceramic, metal-ceramic or inter-metallic composite membranes of the present invention, which meet the United States 1994 and 1998 federal, state and local diesel emission regulations.

Yet another object of the present invention is to initiate and control the regeneration process of a filter using ceramic, metal-ceramic or inter-metallic composites of the present invention, to ensure reliable regeneration without damage to the trap oxidizer.

Another object of the present invention is to make the filter oxidizers less sensitive to regeneration conditions.

A further object of the present invention is to reduce the overall costs of filters used in exhaust systems.

A further object of the present invention is to provide a regeneration system in which a converter or a trap oxidizer could be used without the need for using a catalyst for regeneration.

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Yet another object of the present invention is to provide a heating element integral with a filter, wherein both are highly thermally cyclable and wherein both are ceramic, metal-ceramic or inter-metallic composites.

A further object of the present invention is to provide a heating element which is formed in situ with the filter, both heating element and filter being a ceramic, metal-ceramic or inter-metallic composite.

Yet another object of the present invention is to provide ceramic, metalceramic composite heating element which heats up extremely rapidly.

It is also an object of the present invention to provide a process for producing a coated structure which obviates the dipping involved in the impregnation step in the '737 patent.

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It is a further object of the invention to provide a process for producing a coated structure wherein the impregnation step is less awkward and cumbersome than the impregnation step in the '737 patent.

It is another object of the invention to provide a process for producing a coated structure which avoids the collapse of the "green structure" during processing, as observed in the '737 patent.

It is still another object to provide a process for producing a coated structure which avoids the distortion of the formed article during processing, as observed in the '737 patent.

It is a further object of the invention to provide a process for producing a coated structure which better dissolves certain constituents more easily, such as calcium silicates (cements) such as (CaO)₃. (SiO₂)₂. (H₂O)₃, which lead to a high green and final strength by precipitating out on the deposited surface.

Yet another object of the present invention is to provide a process for producing a single component coated structure for use as a regenerative filter, which structure serves both as a filter and a heating element.

It is also an object of the present invention to provide a process for producing a coated structure for use in exhaust systems, said coating being conductive.

In accordance with the first aspect of the present invention, these is provided, a modulated ceramic, metal-ceramic or inter-metallic composite filter for gaseous, liquid and particulate matter wherein the modules in said filter are ceramic, metal-ceramic or inter-metallic composites, said composites having interconnected or straight through porosity and having been manufactured using micropyretic synthesis, the filter comprising at least two modules. Preferably each module is optimized for extracting different materials.

In accordance with the second aspect of the present invention is provided a regenerator filter comprising a means for filtering and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means.

According to the invention there is provided in a process for producing a porous ceramic, metal-ceramic or inter-metallic composite structure, comprising the steps of providing a slurry comprising ceramic precursors, impregnating a foamed

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polymer shape with said slurry, heating the slurry-impregnated polymer shape to a temperature sufficient to remove said polymer, and heating said ceramic precursors to obtain said ceramic, metal-ceramic or inter-metallic composite structure, an improvement process for producing a coated porous ceramic, ceramic composite or inter-metallic structure, the improvement process comprising the steps of: providing a slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof; impregnating a ceramic, ceramic composite or metal shape with said slurry by (a) fluidizing said slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry; and obtaining a coated porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or by heating said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material so as to cause said nonmicropyretic particulate ceramic, metal, inter-metallic or polymeric material to adhere to said porous ceramic, ceramic composite or metal structure.

According to the invention there is further provided a process for producing a porous ceramic, metal-ceramic or inter-metallic composite structure, comprising the steps of providing a slurry comprising ceramic precursors capable of undergoing combustion synthesis, impregnating a foamed polymer shape with said slurry, heating the slurry-impregnated polymer shape to a temperature sufficient to remove said polymer, and igniting said ceramic precursors to initiate combustion synthesis, thereby obtaining said ceramic, metal-ceramic or inter-metallic composite structure having interconnected porosity and controlled pore size, and improvement process for producing a porous ceramic, metal-ceramic or inter-metallic composite, the improvement process comprising the steps of: providing an improved slurry comprising (A) at least one component selected from the group consisting of (a) at

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least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof; impregnating said polymeric shape with said improved slurry by (a) fluidizing said improved slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said improved slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry; heating the improved-slurry-impregnated polymer shape to a temperature sufficient to remove said polymer; and obtaining a porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or by heating said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material.

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In accordance with a further aspect of the present invention there is provided a heating element in close contact with a porous body which is itself conductive or to which is applied a conductive coating, which porous body can itself function as a heating element, so as to cause it to heat up if a current is applied through said body and which can also function as a filter due to its porosity, wherein the heating element function and the filter function of the porous body is accomplished by a single undivided structure.

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Another aspect of the present invention provides, in a regenerative filter comprising a means for filtering; and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means, the improvement comprising a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise.

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Yet another aspect of the present invention provides a non-regenerative filter means in combination with a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise.

A further aspect of the present invention provides in a modulated filter for gaseous, liquid and particulate matter, wherein the modules in said filter are porous ceramic, metal-ceramic or inter-metallic composite structures, said structures having interconnected porosity and having been manufactured using micropyretic synthesis, the filter comprising at least two modules, the improvement including flexible flaps in between or after the modules, said flaps being made of materials selected from the group consisting of fiber cloth, high temperature wools, and flexible boards, said flaps being susceptible to adherence by particulate fines.

Another aspect of the present invention provides in a regenerative filter comprising a means for filtering; and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means, the improvement comprising fins, metallic fins, or other conductive fins inside the regenerative filter, said fins being used to better distribute heat within the regenerative filter.

An additional aspect of the present invention provides in a modulated filter for gaseous, liquid and particulate matter, wherein the modules in said filter are porous ceramic, metal-ceramic or inter-metallic composite structures, said structures having interconnected porosity and having been manufactured using micropyretic synthesis, the filter comprising at least two modules, the improvement comprising fins, metallic fins, or other conductive fins inside the regenerative filter, said fins being used to better distribute heat within the regenerative filter.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1(a) is a micrograph of an Al₂O₃-SiC ceramic manufactured in accordance with USP 5,279,737, Figure 1(b) is an enhanced micrograph of the ceramic of Figure 1(a);

Figure 2 is a schematic of Filter I as described herein;

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Figure 3 is a schematic of modulated Filter II as described herein;

Figure 4 is a schematic of the test setup used herein for testing filters;

Figure 5 is a micrograph of the filter paper used to collect the exiting material after filtration by a prior art filter;

Figure 6 is a micrograph of the filter paper used to collect the exiting material after filtration by a single module of the present invention;

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Figure 7 is a micrograph of the filter paper used to collect the exiting material by a modulated filter in accordance with the present invention;

Figure 8 shows two filters, with one and two heating elements formed in-situ;

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Figure 9 shows a modulated filter comprising four modules, two with no heating elements, one with one heating element and one with two;

Figure 10 shows a filter as incorporated within a casing specifically adapted to be fitted in a land based vehicle;

Figure 11 shows perspective views of the casings having filters incorporated therein, specifically adapted to be fitted in a land based vehicle (the filters are not visible in this view);

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Figure 12 shows a perspective view of a casing having filters incorporated therein, specifically adopted to be fitted to a 2.5 liter diesel engine, automobile or otherwise; and

Figure 13 is a graph of temperature versus resistivity of HR-1550, the heating element material used in Example 1.

DETAILED DESCRIPTION OF THE INVENTION

The preferred embodiments of the present invention will now be described in greater detail.

5 First Embodiment

This aspect of the present invention provides a modulated ceramic, metal-ceramic or inter-metallic composite filter for gaseous, liquid and particulate matter, wherein the modules in the filter are porous ceramic, metal-ceramic or inter-metallic composites, the modules having interconnected porosity and having been manufactured using micropyretic synthesis, wherein the filter comprises at least two such modules.

Optionally, the modulated filter of the present invention also comprises a catalyst, the catalyst being applied to the filter by coating, impregnating and combinations thereof; and wherein the catalyst reacts or is reactive under conditions of vacuum, room temperature, increased temperature, pressure or combinations thereof.

Optionally, each module of the filter is optimized for extracting a different material, particularly, particulates, carbon particles, NO_x, CO, CO₂, SO₂, hydrocarbons, and combinations thereof.

Also, preferably, the composite is reticulated. "Reticulated" as used herein refers to a porous 3-dimensional structure without straight-through channels.

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The greater the roughness of a filter material, the better the performance of the filter. Therefore, it is preferred that the composite has a rough surface. A "rough" surface as used herein may be understood as a surface with a high frequency of peaks and valleys, the peaks and valleys creating spaces suited for particle trapping. See Figures 1(a) and (b), which illustrate a typical "rough" composite used as modules in the present embodiment. The roughness of the composite can be enhanced either chemically or mechanically.

Of the several materials disclosed in the '737 patent, it is preferred that the composite (even in its heating element form), comprises a material selected from the group consisting of borides or aluminides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; aluminides (except of aluminum), carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, iron, molybdenum, vanadium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-titanium boride-titanium nitride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum silicidealuminum oxide; molybdenum boride-aluminum oxide; chromium carbide-aluminum oxide; vanadium nitride-aluminum oxide, aluminides of nickel, compounds of platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

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Comparative Example

Two alumina-silicon carbide (Al₂O₃-SiC) filters were made of porous reticulated ceramic fabricated by the process of US Patent 5,279,747. The first filter (I) was made by using a ten pores per inch, cylindrical shaped reticulated ceramic having a 4" diameter and 3" height. The ceramic monolith was packed in a steel casing as shown in Figure 2. See also, Figure 10. The second filter (II) was made by stacking nine, ten pores per inch reticulated ceramic discs of 2" diameter and 1/2" thickness, alternating them with a steel ring 1/2" long to separate the ceramic discs in a 9" long steel casing, making a modular filter (Figure 3).

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The two filters for particulate matter were tested on a diesel engine to compare their performance with the diesel filters available in the market. Engelhard's 3DVC-

PTX and 4DVC-PTX diesel filters were used for the comparison. These filters have a ceramic monolith with square shaped cells, passing straight through the whole body, with a mean wall thickness of 0.15mm and 14 pores per inch. This ceramic monolith is manufactured by Corning Inc. The setup for the test comprised of a 22HP four stroke diesel engine made by Lister Petter and a paper holder with a filter paper to catch the particles from the engine exhaust. See Figure 4. The setup was in the open at an ambient temperature of 40°F. All the four filters I, II, 3DVC and 4DVC were successively tested. Each of these filters were connected to the engine exhaust pipe as shown in the set up. The filter paper was uniformly sprayed with water to enable the exhaust particles to stick to the surface. The engine was started and was run for two minutes for each filter.

The gain in weight of the paper, which was used for collecting the particles from the exhaust, and visual inspection, were used as the criterion for determining the performance of the filters. Filter I and Filter 4DVC had exactly the same dimensions. The gain in weight of the filter paper due to the particles collected from the exhaust of filter I was 0.01g, where as that from filter 4DVC was 0.03g. Also the paper used the filter 4DVC was much darker with more black spots than the one used with filter I. See Figure 5 which is a micrograph of the filter paper used with 4DVC; Figure 6 which is a micropyretic of the filter paper used with filter I; and Figure 7 which is a micrograph of the filter paper used with filter II. Thus, it is clearly demonstrated that filter I is much superior in performance as compared to filter 4DVC.

Filter II was the best filter among the four filters tested. See Figures 5, 6 and 7. The gain in weight was negligible and the paper was slightly yellowed with no black spots, suggesting a high degree of filtration.

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Second Embodiment

The second aspect of the present invention provides a regenerative filter comprising: a means for filtering, and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means.

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Preferably, the means for filtering comprises at least one porous composite having interconnected porosity and having been manufactured using micropyretic synthesis. Preferably, the means for regenerating is a heating element. Optionally, the regenerating means may also be a catalyst. Even more preferably, the heating element/catalyst can be a porous composite.

The filter/heating element preferably comprises a compound selected from the group consisting of metallic material, molybdenum silicides, Fe-Cr-Al, Ni-Cr, SiC and combinations thereof.

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The filter/heating element preferably comprises a material selected from the group consisting of borides or aluminides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; aluminides (except of aluminum), carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, iron, molybdenum, vanadium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride: aluminum oxide-titanium boride-titanium nitride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum silicidealuminum oxide; molybdenum boride-aluminum oxide; chromium carbide-aluminum oxide; vanadium nitride-aluminum oxide, aluminides of nickel, compounds of platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

Preferably, the regenerating means (the heating element or catalyst) is formed in situ with the composite filter.

Preferably, the composite is reticulated. The catalyst. if present, is applied to the filter by coating, impregnating, and combinations thereof.

Example 1

A reticulated filter with a pore size of 10 pores per inch (pore sizes ranging from 10-80 pores per inch are most preferred for the practice of the invention), manufactured according to USP 5,279,737 was made, except that a 3 mm high resistivity heating element manufactured by Micropyretics Heaters International under the trade name HR-1550 with terminals was incorporated into the reticulated filter prior to combusting the sample. See, Figure 12 which is a resistivity to temperature graph for HR-1550, showing that the resistivity of HR-1550 increases with temperature. "High" resistivity means 50-5000 μ ohm-cm, whereas "low" resistivity is understood to be around 1 μ ohm-cm. "Low" resistivity heating elements require in excess of 300 amps to be heated up quickly, but a typical 12V automobile battery can only generate less than 100 amps. Therefore, it is important that a high resistivity heating element be used. Materials which may be used as high resistivity heating elements are: molybdenum disilicide, silicon carbide, tungsten silicide, zirconium oxide, lanthanum chromite, graphite, compounds and composites thereof.

See, Figure 8 which shows two filters, with one and two heating elements formed in-situ. The final material of the filter was a composite of Al₂O₃/SiC when used as a particle trap for exhaust gases was found to effectively trap particulates. The heating element could be energized during use and after use as a particle trap to burn off the carbon deposit. Many such filters of size three inches in diameter and two inches in depth could be used in tandem to give a modulated filter of greater length. See, Figure 9, which shows a modulated filter comprising four modules, two with no heating elements, one with one heating element and one with two. Figure 10 shows a filter as incorporated within a casing specifically adapted to be fitted in

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a land based vehicle. Figure 11 shows perspective views of the casings having filters incorporated therein, specifically adapted to be fitted in a land based vehicle (the filters are not visible in this view).

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Example 2

A filter with a porous size of five pores per inch, otherwise the same as example one.

Example 3

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Same as example one expect the filter had various slurry coatings of nickel compounds (both combustible and non-combustible slurry coatings) applied thereto.

Example 4

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Same as example one expect the filter had various coatings of platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof, applied thereto.

Example 5

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The heating element was made of silicon carbide, otherwise the same as example 2.

Example 6

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The filter was made according to Example 2, but heating element was of a conventional metallic material such as Fe-Cr-Al alloy or NiCr alloy. However, the heating elements made from molybdenum disilicides were found preferable.

Example 7

A cylindrical shaped membrane filter (Micropyretics Heaters International's DPF)¹¹⁴, having 2.8 inches diameter, 3 inches length (several Al₂O₃/SiC membranes as in Example 1 were stacked together to yield a modulated filter of 3 inches length)

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and 10 pores per inch, was used for Example 7. This filter had a U shaped HR-1550 element sandwiched in the length of the filter.

Initially, emission tests were conducted on an as is 1981 Volkswagon Rabbit, with a 1.6L diesel engine. A BEAR smokemeter was used to measure the opacity (in m⁻¹) of the exhaust gases of the Volkswagon Rabbit and a BEAR tachometer was used to measure the revolutions per minute of the engine (RPM) of the same. A percentage opacity and density of particulates was measured. The smokemeter was connected using a hose to the vehicle exhaust pipe and the tachometer was connected to the fuel pipe to the engine. This apparatus was interfaced with an IBM Intel 486 based computer to collect real time data. The car was started and warmed for 1/2 hour before the tests were conducted.

A standard certification test procedure was used to measure the emission. The procedure involves a three step process. First, the opacity of the exhaust is measured under idle conditions, i.e. when the engine is just turned on, for a fixed amount of time. Then, the engine is immediately accelerated to the maximum RPM and maintained for a given time, after which the engine is deaccelerated to the idle state. These steps are repeated up to ten times to get the best four results, which are used to obtain the average opacity of the exhaust. The computer decides when it has received at least four uniform tests. If the first four are not uniform, then the computer asks for further tests until either four satisfactory results are obtained or a minimum of ten measurements are taken, whichever occurs first. The results given below in Table I are the values obtained at around the highest RPM of the car (approximately 5300), without any filter attached to the car.

Next, the filter (modulated and regenerative) was installed to the exhaust pipe of the car. The opacity test was then repeated. The results are presented in Table II. It was noted that the current drawn by the heating element was of the order of 25 amps, which is well below the 100 amps easily generated by a 12V battery.

As noted above for all tests, at least four high RPM excursions are required by the computer. It was noted that when a filter was employed the computer was always satisfied with doing four tests. However when no filter was present the computer had to ask for ten tests.

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As is obvious, when the DPF™ membrane filter is used there is a dramatic improvement in the exhaust gas emissions over the case when no filter is used. Also, the engine ran much more consistently and uniformly when a DPF™ filter was used. When calculated as the weight of particles reduced per unit volume the results show an average reduction of 0.2 g/m³ when the filter is used.

engine without filter

TABLE I

TEST 8:54 h	ENGINE SPEED RPM	% OPACITY	OPACITY m ⁻¹	DENSITY OF PARTICULATES g/m³
1 .	5043	74.4	3.07	0.514
2	5047	81.0	3.75	0.626
3	5071	83.1	4.01	0.669
4	4935	63.8	2.30	0.395

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Average:			3.28		0.551
•	•	-			
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TEST 9:03 h	ENGINE SPEED RPM	% OPACITY	OPACITY m ⁻¹	DENSITY OF PARTICULATES g/m³
. 1	5334	77.4	3.40	0.559
2	5332	84.4	4.25	0.691
3	5334	79.9	3.67	0.609
4	5335	82.3	3.96	0.648

Average:

3.82 0.627

TABLE II using diesel particulate filter (regenerative and modulated) at the end of the exhaust

exnaust				
TEST 10:20 h	ENGINE SPEED RPM	% OPACITY	OPACITY m ⁻¹	DENSITY (PARTICULAT g/m³
1	4991	39.0	1.14	0.187
2	5073	46.2	1.42	0.234
3	6000	34.9	0.99	0.162
4.	5010	36.8	1.05	0.174
Average:		•	1.15	0.189
TEST 10:24 h	ENGINE SPEED RPM	% OPACITY	OPACITY m ⁻¹	DENSITY O PARTICULAT g/m³
. 1	4935	35.7	1.01	0.168
2 .	4799	38.2	1.10	0.181
3	5051	37.3	1.07	0.174-
4	4980	40.4	1.19	0.193
Average:			1.09	0.179-
TEST 10:28 h	ENGINE SPEED RPM	% OPACITY	OPACITY m ⁻¹	DENSITY [*] O PARTICULATI g/m ³
1	6000	34.6	0.97	0.162
2	4955	33.3	0.93	0.150
3	4975	35.2	1.00	0.162
4	4941	36.0	1.03	0.168
Average:			0.98	0.161
TEST 10:32 h	ENGINE SPEED RPM	% OPACITY	OPACITY m ⁻¹	DENSITY OF PARTICULATE g/m³
1	5165	32.0	0.89	0.144
2 .	5057	33.2	0.93	0.150

3	5005	37.0	1.06	0.174
4	5084	37.3	1.07	0.174

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Advantageously, the modulated filter aspect of the present invention may be used in a land-based vehicle, water-based vehicle, in power generation equipment or in an industrial engine. Similarly, the regenerative filter aspect of the present invention may also be used advantageously in a land-based vehicle, water-based vehicle, in power generation equipment or in an industrial engine. More generally, the modulated filter aspect of the present invention may be used in a regenerative exhaust system. Similarly, the regenerative filter aspect of the present invention may also be used in a regenerative exhaust system. Analogously, the modulated filter aspect can be used in a catalytic converter.

The modulated filter and/or the regenerative filter, may be used in a diesel engine in combination with a preheater for heating the exhaust gases prior to the gases entering the filter.

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In a regenerative filter comprising a means for filtering; and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means, an improvement is disclosed which comprises a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise.

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Yet another aspect of the present invention provides a non-regenerative filter means in combination with a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise. The above aspect may be further enhanced by including a means for heating the fluid entering the valve.

A further aspect of the present invention provides in a modulated filter (as shown in Figure 2), for gaseous, liquid and particulate matter, wherein the modules

in said filter are porous ceramic or ceramic composite structures, said structures having interconnected porosity and having been manufactured using micropyretic synthesis, the filter comprising at least two porous ceramic or ceramic composite modules, an improvement including flexible flaps in between or after the modules, said flaps being made of materials selected from the group consisting of fiber cloth, high temperature wools, and flexible boards, said flaps being susceptible to adherence by particulate fines. The flaps of the above improvement may preferably be flexible enough so that they are displaced if the flow rate of the fluid to be filtered increases beyond a specified value, but which flaps remove fine particulates at lower flow rates.

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Another aspect of the present invention provides, in a regenerative filter comprising a means for filtering; and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means, an improvement comprising fins, metallic fins, or other conductive fins inside the regenerative filter, the fins being used to better distribute heat within the regenerative filter.

An additional aspect of the present invention provides in a modulated filter for gaseous, liquid and particulate matter, wherein the modules in said filter are porous ceramic or ceramic composite structures, said structures having interconnected porosity and having been manufactured using micropyretic synthesis, the filter comprising at least two porous ceramic or ceramic composite modules, the improvement comprising fins, metallic fins, or other conductive fins inside the regenerative filter, said fins being used to better distribute heat within the regenerative filter.

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Preferably the modulated filters and/or the regenerative filters of the present invention, may be specially (with or without a catalyst), adapted to utilize the heat released from the filters elsewhere in the land-based vehicle, water-based vehicle, power generation equipment or industrial engine, in which the filters are fitted. In such a case, the filter is adapted to receive external combustible matter for combustion to generate additional heat. The combustible matter may be carbon,

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gasoline products, hydrocarbons, metals or any matter which reacts with a positive enthalpy change. The modulated filters and/or the regenerative filters of the present invention are designed to increase the residence time of the combustible matter such as carbon particles, so as to allow the combustible matter to be brought to ignition temperature and thenceforth to be combusted. The modulated filters and/or the regenerative filters of the present invention cause the increased residence time by (1) trapping the combustible matter and (2) providing a tortuous path for travel by the gas carrying the combustible matter. The importance of a higher residence time is. reduced by a hotter substrate (the cell walls of the modulated filters and/or the regenerative filters), and/or a hotter means for heating, such as a heating element. Gradually, the cell walls of the modulated filters and/or the regenerative filters get coated with the combustible matter. Combustion of the combustible matter is initiated by ignition, which occurs due to radiation from the means for heating, such as a heating element. Following ignition, spontaneous combustion may occur if the combustible matter is well deposited, which would then proceed along the walls of the modulated filters and/or the regenerative filters, requiring no further heat from the means for heating. When the combustible matter burns it radiates heat to the cell walls of the modulated filters and/or the regenerative filters, which can cause the walls to radiate back and burn more particles or be useful in maintaining the combustion process.

Preferably the composites in the modulated and/or regenerative (with or without a catalyst) filters, may be in the form of porous membranes. In such a case, the filters may be advantageously used in furnaces used for producing wax and the like.

Preferably the filters of the present invention can attain temperatures of up to 1200°C. Preferably, the filters of the present invention further include a means for gauging the aging of the catalytic converter.

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Preferably the filters when fitted in a land based vehicle, water-based vehicle, power generation equipment or industrial engine, also include a device selected from

an ignitor, a spark producing means, a heating element, a laser means, a means for inducing a chemical reaction and combinations thereof. The above devices may be in addition to or instead of the filter. Preferably, the spark producing means causes intermittent or pulsed sparks or discharges.

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In accordance with a further aspect of the present invention, a means for heating is provided such as a heating element being high resistivity and/or high emissivity, an ignitor, a laser, a spark producing means, a means for inducing a chemical reaction and combination thereof, in land-based vehicles, water-based vehicles, power generation equipment or an industrial engine.

Preferably when the above heating devices are used alone or together with a filter, a surface is not required for combustion of particulates and/or exhaust gases, as is required in a catalytic converter.

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Preferably the regenerative filter of the present invention further includes one or more heating element and an electrical terminal which may or may not be of the same material as the heating element. Preferably a plurality of heating elements are included in combination with a ballast.

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Preferably the means for regenerative in a regenerative filter is a thin film resistor, such as the conductive coatings applied on to the filters as will be described in greater detail below.

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Preferably the means for regenerating includes a device which acts as a solid state switch. The switch may be formed of a piezo electric substance. The piezo electric substance is preferably a spinel ferrite. The ferrite is preferably barium titanate and/or strontium titanate. The titanates may or may not be doped. The solid state switch like device may be used in combination with a heating element. The solid state switch like device may be formed of an electro-optic ceramic substance.

Preferably the means for regenerating includes a device such as thyristors and/or varistors. Also preferably the device may be formed of a substance having a positive temperature coefficient.

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Preferably the filters (modulated and/or regenerative) of the present invention further include an energy storage devoie. This devoie may preferably be an inductor or a capacitor. In prior art filters/catalytic converters, used in gasoline engines especially, start up is the worst period from the standpoint of pollution. The filter/catalytic converter is typically "cold" and therefore not much combustion/purification occurs. By including an energy storage devoie which is charged during normal use, the stored energy is available for use during the start up period. By connecting the device so that upon starting the device releases energy to the filter, this problem of low energy is obviated and effective filtration and combustion occurs during start up.

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In accordance with another aspect of the present invention, there is provided a means for separating particles with differing densities wherein said separating means is integrally connected with a heating element. Preferably the means for separating is a venturi tube or a vortex tube. The means for separating may or may not be micropyretically synthesized.

Membrane Technology

The filters/modules used in the above-described two embodiments of the present invention may preferably be in the form of porous ceramic, metal-ceramic or inter-metallic membranes. Such membranes and their methods of manufacture are described in greater detail below. These membranes may be thin, two dimensional bodies with a single layer membrane having a thickness within the range of 50 microns to 10mm or can also be much thicker being generally cylindrical in shape. It is believed that the pores in present membranes can range in size from 0.1 micron to 500 microns. Because the pores have different shapes, pore size is usually determined by converting the pore area into an equivalent circular area. Pore densities can be within the range of 20 to 80%.

The basic method for making or synthesizing a porous membrane includes preparing a slurry having at least one micropyretic substance and at least one liquid carrier for the micropyretic substance. The slurry is preferably applied to the surface of a substrate or article and allowed to dry on the surface into a green form of the membrane. The green form of the membrane is then fired or burned according to micropyretic principles in order to form a porous membrane. It is often desirable to modify the slurry with the addition of other substances, referred herein as diluents. The slurry could have a consistency ranging from very fluid to very powdery. Such slurries according to the present invention can include various combinations of the following constituents:

Micropyretic substances or agents. These agents are typically particles, fibers, or foils of materials such as Ni, Al, Ti, B, Si, Nb, C, Cr₂O₃, Zr, Ta, Mg, Zn, MgO, ZnO₂, ZrO₂, TiO₂, B₂O₃, Fe or combinations thereof which may react to yield both heat as well as clean and nascent products from the combustion. Typical reactions could be for example $Cr_2O_3 + Al + B$, Ni + Al or Ti + B or C + Al +SiO₂, etc., which react spontaneously to give CrB₂, Ni₃Al or TiB₂ or SiC and Al₂O₃, respectively, with a large release of heat. The adiabatic temperature of such a micropyretic reaction could be as high as 6,500°K. Tables I, II, and III give a partial listing of micropyretic reactions (reactants and products) and the approximate amount of heat released in each reaction. $\Delta H(KJ/mole)$ is the enthalpy release for the reaction and T_{ad} K is the adiabatic temperature which is expected to be reached in such reactions. The enthalpy release and the adiabatic temperature are not precisely known for all the reactions in Tables I-III. However, all of the reactions listed are believed to be sufficiently exothermic. Table IV gives a list of some micropyretic reactions and stoichiometries. It is believed that mixtures of the constituents of Table I-IV are also possible along with the addition of diluents which could often be the product itself or other materials in powder, foil, fiber or other form of a predetermined size. It is also believed that each of the reactants and products of the reactions listed in Tables I-III could function as diluents.

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TABLE 1
FORMATION OF REFRACTORY COMPOUNDS

REACTION	ΔH(KJ/m le)	T _{ad} l
$Ti + 2B = TiB_2$	-293	319
$Zr + 2B = ZrB_2$	-263.75	331
$Nb + 2B = NbB_2$	-207.74	240
Ti + B = TiB	-158.84	335
$Hf + 2B = HfB_2$	-310.15	352
$Ta + 2B = TaB_2$	-193.53	337
Ti + C = TiC	-232	321
$3B_2O_3 + 10A1 + 3TiO_2 = 3TiB_2 + 5A1_2O_3$		400
$B_2O_3 + 5Mg + TiO_2 = TiB_2 + 5MgO$		
$B_2O_3 + 5Zn + TiO_2 = TiB_2 + 5ZnO$		
$2B_2O_3 + 5Zr + 2TiO_2 = 2TiB_2 + 5ZrO_2$		·
Si+C=SiC	-65.3	180
W+C=WC	-40.6	100
V+C=VC	-102	240
Nb+C=NbC	-140	280
$2Nb+C=Nb_2C$	-186	260
Zr + C = ZrC	-202.9	344
Hf+C=HfC	-218.6	390
Ta+C=TaC	-142.9	270
$2Ta + C = Ta_2C$	-202.7	266
$4A1 + 3C = A1_4C_3$	-208.8	167
$2Mo+C=Mo_2C$	-50	100
$4B+C=B_4C$	-71	100
$V + 2B = VB_2$		267
La+6B=LaB ₆	·	280
W+B=WB		170

	REACTION	ΔH(KJ/mole)	TadK
	$2W + B = W_2B$	-87	1400
	$Cr + 2B = CrB_2$	-94.1	2470
	U+4B=UB4		1770
	$Mo + 2B = MoB_2$		1800
5	Mo+B=MoB	-112.4	1800
	$A1 + 12B = A1B_{12}$	-200.6	
	$Ti + 1/2N_2 = TiN$	-336.6	4900
·	$3Ti + NaN_3 = 3TiN + Na$		
	$3Si + 2N_2 = Si_3N_4$	-738.1	4300
10	$3Si + 4NaN_3 = Si_3N_4 + 4Na$		
	$Hf + 1/2N_2 = HfN$	-368.7	5100
	$B+1/2N_2=BN$	-254.1	3700
	$Zr + 1/2N_2 = ZrN$		4900
	$Ta + 1/2N_2 = TaN$	-252.1	3360
15	$2Ta + 1/2N_2 = Ta_2N$	-272.5	3000 -
	$V+1/2N_2=VN$	-216.9	3500
	$A1 + 1/2N_2 = A1N$	-302.5	2900
	$La + 1/2N_2 = LaN$	-299.4	2500
	$3Be + N_2 = Be_3N_2$	-564.0	3200
20	$U+1/2N_2=UN$	-286.8	3000
	$3Mg + N_2 = Mg_3N_2$	-416.1	2900
Ŀ	$Nb + 1/2N_2 = NbN$	-237.8	3500
	$2Nb + 1/2N_2 = Nb_2N$	-248.3	2670

TABLE II
FORMATION OF INTERMETALLICS

REACTION	ΔH(KJ/mole)	$T_{ad}K$
Ti + Ni=TiNi	-278.2	1773
Ti + Pd=TiPd	-103.4	1873
Ni + A1=NiA1	-118.4	1911
Ti + Al = TiAl	-72.8	1654
Ti+Fe=TiFe	-40.6	1110
$5Ti + 3Si = Ti_5Si_3$	-578.9	2500
$Ti + 2Si = TiSi_2$	-134.2	1800
Ti+Si=TiSi	-130	2000
$Mo + 2Si = MoSi_2$	-131.7	3190
$W + 2Si = WSi_2$	-92.9	1500
$5V + 3Si = V_5Si_3$	-461.9	3190
$Ta + 2Si = TaSi_2$	-119.1	1800
Zr+Si=ZrSi	-155	2100
$Zr + 2Si = ZrSi_2$	-153.8	2100
$5Zr + 3Si = Zr_5Si_3$	-147.6	2800
$Nb + 2Si = NbSi_2$	-137.9	1900
$2Ni + SiC = Ni_2Si + C$	-76	
$3Ni + 2SiC = Ni_3Si_2 + 2C$	-98	4
Cd+S=CdS	-149.2	2000
Mn+S=MnS	-213.2	3000
$Mo + 2S = MoS_2$	-275	2300
Ni+2S=NiS ₂		
Ni+P=NiP		
Nb+P=NbP	·	
$3Ni + A1 = Ni_3A1$	-153.2	
$3Ni_3A1_2 + 9Ni = 6Ni_3A1$		

	REACTION	ΔH(KJ/mole)	$T_{ad}K$
	Ni+3A1=NiA1 ₃	-162	
	$3Ni + 2A1 = Ni_3A1_2$	-282.6	
Ŀ	$Ti + 3A1 = TiA1_3$	-142.1	1517
L	Cu + A1 = CuA1		899
L	Cu+2A1=CuA1 ₂		
4	$4Cu + 3A1 = Cu_4A1_3$:	
3	$3Cu + 2A1 = Cu_3A1_2$		
g	$9Cu + 4A1 = Cu_9A1_4$		
I	Fe+A1=FeA1	-18	
3	3Fe+A1=Fe ₃ A1	-31.8	
2	$Zr + A1 = ZrA1_2$		1918
F	Pd+A1=PdA1		2579
1	$\Gamma i + N i = T i N i$	-66.5	1552
1	Γi+Pt=TiPt	-159.5	-
Γ	Γi+Co=TiCo	-47.7	1723
C	Co+A1=CoA1	-110.4	1901
5	$50Ti + (50-x)Ni + xPd = Ti_{50}Ni_{50-x}Pd$		
5	$0\text{Ti} + (50-x)\text{Ni} + x\text{Fe} = \text{Ti}_{50}\text{Ni}_{50-x}\text{Fe}$		
5	$60Cu + (50-x)A1 + xNi = Cu_{50}A1_{50-x}Ni$		•
5	$0Cu + (50-x)A1 + xMn = Cu_{50}A1_{50-x}Mn$		

TABLE III FORMATION OF COMPOSITES

REACTION	ΔH(KJ/mole)	$T_{ad}K$
$Fe_2O_3 + A1 = A1_2O_3 + 2Fe$	-836	3753
$Cr_2O_3 + A1 = A1_2O_3 + 2Cr$	-530	2460
$3Cr_2O_3 + 6A1 + 4C = 2Cr_3C_2 + 3A1_2O_3$		6500 .
$0.86\text{Ti} + 1.72\text{B} + 1.48\text{A}1 = 0.86\text{TiB}_2 + 1.48\text{A}1$	-293	1450
Ti + C + 0.68Ni = TiC + 0.68Ni	-232	1370
$Zr + 2B + Cu = ZrB_2 + Cu$	-263.75	1100
$4A1 + 3SiO_2 + 3C = 2A1_2O_3 + 3 SiC$		
$3Fe_3O_4 + 8A1 = 4A1_2O_3 + 9Fe$	-816	3509
$3NiO + 2A1 = 2A1_2O_3 + 3Ni$	-928	3546
$3MnO_2 + 4A1 = 2A1_2O_3 + 3Mn$	-878	4123
$3SiO_2 + 4A1 = 2A1_2O_3 + 3Si$		
$3\text{TiO}_2 + 4\text{A}1 = 2\text{A}1_2\text{O}_3 + 3\text{Ti}$		
$Fe_2O_3 + 3Mg = 3MgO + 2Fe$	-323	3076
$Fe_3O_4 + 3Mg = 4MgO + 3Fe$	-316	3184
$Cr_2O_3+3Mg=3MgO+2Cr$	-221	2181
NiO+Mg=MgO+Ni	-353	2579
$3MnO_2 + 2Mg = 2MgO + Mn$	-337	3665
$2Fe_2O_3 + 3Si = 3SiO_2 + 4Fe$	-311	2626
$Fe_3O_4 + 2Si = 2SiO_2 + 3Fe$	-298	1808
$2NiO + Si = SiO_2 + 2Ni$	-373	2602
$2MnO_2 + Si = 2SiO_2 + Mn$	-339	3024
$2Fe_2O_3 + 3Ti = 3TiO_2 + 4Fe$		
$2Fe_2O_3 + 3Zr = 3ZrO_2 + 4Fe$		
$2Cr_2O_3 + 3Zr = 3ZrO_2 + 4Cr$		<u>.</u>
$Ti + 2B + aTiB2 + bCu = (a+1)TiB_2 + bCu$		

TABLE III (cont'd)

	REACTION	ΔH(KJ/mole)	$T_{ad}K$
	$CrO_3 + Cr_2O_3 + 6A1 + 2C + 3NiO = $ $Cr_3C_2 + 3A1_2O_3 + 3Ni$		· · · · · · · · · · · · · · · · · · ·
5 ,	$Nb_2O_5 + A1_2Zr + vA1_2O_3 = 2Nb + ZrO_2 + A1_2O_3 + vA1_2O_3$	·	**************************************
	$Nb_2O_5 + 2A1 + Zr + vA1_2O_3 =$ $2Nb + ZrO_2 + A1_2O_3 + vA1_2O_3$		
	$Nb_2O_5 + 10/3A1 + \Phi ZrO_2 + vA1_2O_3 = 2Nb + \Phi ZrO_2 + 5/3A1_2O_3 + vA1_2O_3$		
10	$B_4C + (x+5)Ti = xTiB + 4TiB + TiC$		
	$2\text{Ti} + \text{C} + 2\text{B} = \text{TiB}_2 + \text{TiC}$		
	$38B + TiAl_3 = TiB_2 + 3AlB_{12}$		
	$3\text{TiO}_2 + 4\text{Al} + 3\text{C} = 3\text{TiC} + 2\text{Al}_2\text{O}_3$		2300
	$9\text{TiO} + 11\text{C} + 2\text{TiAl}_3 = 11\text{TiC} + 3\text{Al}_2\text{O}_3$		
15	$3SiO_2 + 4Al + 3C = 3SiC + 2Al_2O_3$		
	$3ZrSiO_4 + 4Al + 3C = 3ZrO_2 + 3SiC + 2Al_2O_3$		
	$WO_3 + 2Al + C = WC + Al_2O_3$:
	$2B_2O_3+4AI+C=B_4C+2AI_2O_3$		
	$2ZrO_2 + 4AI + C = ZrC + 2AI_2O_3$		
20	$2\text{MoO}_3 + \text{Al} + 3\text{C} = 3\text{Mo}_2\text{C} + 2\text{Al}_2\text{O}_3$		· .
	$3B_2O_3 + 10Al + 3TiO_2 = 3TiB_2 + 5Al_2O_3$		4000
	$6B+4Al+3TiO_2=3TiB_2+2Al_2O_3$		4000
	$10B_2O_3 + 3TiO_2 + 2B + 8TiAI_3 = $ $11TiB_2 + 12AI_2O_3$		
25	$9\text{TiO}_2 + 26\text{B} + 4\text{TiAl}_3 = 13\text{TiB}_2 + 6\text{Al}_2\text{O}_3$		
•	$3\text{Ti} + 3\text{B}_2\text{O}_3 + 2\text{TiAl}_3 = 3\text{TiB}_2 + 3\text{Al}_2\text{O}_3$		
	$B_2O_3 + ZrO_2 + 10/3Al = ZrB_2 + 5/3Al_2O_3$	-	2400
	$MoO_3+2AI+B=MoB+AI_2O_3$	-1117.3	4000

TABLE III (cont'd)

$3HfO_2 + 4Al + 6B = 3HfB + 2Al_2O_3$		
REACTION	ΔH(KJ/mole)	T _{ad} K
$3V_2O_5 + 10Al + 3N_2 = 6VN + 5Al_2O_3$		4800
3TiO2 + 2Al + NaN3 = 3TiN + Al2O3 + Na	·	
$3\text{TiO}_2 + 4\text{Al} + 1.5\text{NaCN} =$ $3\text{TiC}_{0.5}\text{N}_{0.5} + 2\text{Al}_2\text{O}_3 + 1.5\text{Na}$		
$Ti + 0.5C + 0.167NaN_3 = TiC_{0.5}N_{0.5} + 0.167Na$		·
$MoO_3 + 2Al + 2Si = MoSi_2 + Al_2O_3$		3300
$2Si_{3}N_{4}+4B_{2}O_{3}+9Al_{2}O_{3}=8BN+3(3Al_{2}O_{3}+2SiO_{2})$		4800
$TiO_2 + 2Mg + C = TiC + 2MgO$		·
$SiO_2 + 2Mg + C = SiC + 2MgO$	2300	
$2B_2O_3 + 6Mg + C = B_4C + 6MgO$		·
$B_2O_3 + 5Mg + TiO_2 = TiB_2 + 5MgO$	·	
$MoO_3 + 3Mg + B = MoB + 3MgO$		•
$M_0O_3 + Mg + 2Si = M_0Si_2 + 3MgO$		
$TiO_2 + Zr + C = TiC + 2ZrO_2$		
$SiO_2 + Zr + C = SiC + ZrO_2$		0
$2B_2O_3 + 5Zr + 2TiO_2 = 2TiB_2 + 5ZrO_2$		
$2MoO_3 + 3Zr + 2B = 2MoB + 3ZrO_2$		
$2MoO_3 + 3Zr + 4Si = 2MoSi_2 + 3ZrO_2$		
$1/2V_2O_5 + 11/3B = VB_2 + 5/6B_2O_3$	·	2700
$1/2Cr_2O_3 + 3B = CrB_2 + 1/2B_2O_3$		1900
$2M_0O_3 + 5B = M_02B + 2B_2O_3$		3000
$1/2Fe_2O_3 + 2B = FeB + 1/2B_2O_3$		2400
$1/2\text{Fe}_2\text{O}_3 + 4\text{B} + 2\text{Fe} = 3\text{FeB} + 1/2\text{B}_2\text{O}_3$		1800
$2M_0O_3 + 10M_0 + 24B = 11M_0B_2 + B_2O_3$		2200

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TABLE III (cont'd)

$PbO + MoO_2 = PbMoO_3$	1340
$PbO_2 + WO_2 = PbWO_4$	2000

TABLE III (cont'd)

$BaO_2 + SiO = BaSiO_3$	1880
$BaO_2 + TiO = BaTiO_3$	1980
$PbO_2 + TiO = PbTiO_3$	1440
$MnO_2 + TiO = MnTiO_3$	1630
$MnO_2 + TiO = MnSiO_3$	1540
$Si + N_2 + Si_3N_4 + (SiO_2)_z + AlN = Si_{6-z}Al_zO_zN_{8-z}$	2673

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TABLE IV

SAMPLE MICROPYRETIC REACTIONS

AND STOICHIOMETRIC WEIGHTS

REACTION	WEIGHT %
Ni+A1=NiA1	Ni: 68.5, A1: 31.5
$3Ni + A1 = Ni_3A1$	Ni: 86.7, A1: 13.3
$3Cr_2O_3 + 6A1 + 4C = 2Cr_3C_2 + 3A1_2O_3$	Cr ₂ 0 ₃ : 69, A1: 24, C: 7
$MoO_3 + 2A1 + B = MoB + A1_2O_3$	MoO ₃ : 69, A1: 25.9, B: 5.1
$MoO_3 + 2A1 + 2Si = MoSi_2 + A1_2O_3$	Mo0 ₃ : 57, A1: 21, Si: 22
$Ti + 2B = TiB_2$	Ti: 68.9, B: 31.1
5Ti+3Si+Ti ₅ Si ₃	Ti: 74, Si: 26
$Nb+2A1=NbA1_2$	Nb: 63.3, A1: 36.7
$Zr + 2B = ZrB_2$	Zr: 80.8, B: 19.2
$Nb + 2B = NbB_2$	Nb: 81.1, B: 18.9
$Fe_2O_3 + 2A1 = A1_2O_3 + 2Fe$	Fe ₂ 0 ₃ N: 74.7, A1: 25.3
$Cr_2O_3 + 2A1 = A1_2O_3 + 2Cr$	Cr ₂ 0 ₃ : 73.8, A1: 26.2
$0.86\text{Ti} + 1.72\text{B} + 1.48\text{A}1 = 0.86\text{TiB}_2 + 1.48\text{ A}1$	Ti: 41.3, B: 18.7, A1: 40
Ti+B=TiB	Ti: 81.6, B: 18.4
Hf+2B=HfB ₂	Hf: 89.2, B: 10.8
$Ta + 2B = TaB_2$	Ta: 89.3, B: 10.7
Ti+C=TiC	Ti: 80, C: 20
Γi+Ni=TiNi	Ti: 44.9, Ni: 55.1
Ti + Pd + TiPd	Ti: 31.0, Pd: 69.0
Γi+A1=TiA1	Ti: 64, A1: 36
Γi+Fe=TiFe	Ti: 46.2, Fe: 53.8
Γi+C+0.68Ni=TiC+0.68Ni	Ti: 48, C: 12, Ni: 40
$Ni+3A1 = NiA1_3$	Ni: 42, A1: 58
$4A1 + 3 SiO_2 + 3C = 2A1_2O_3 + 3 SiC$	A1: 33.29, SiO ₂ : 55.59, C:11

Also included in the referenced slurry used to make the membranes could be the following components:

2) A liquid carrier (i.e., liquid suspending medium) which could be aqueous or non-aqueous and have either a low or high viscosity. The carrier is most often chosen from a group of plasticizers (i.e., binders in suspension) which may include clays of various sorts such as bentonite, fused silica, kaolinite and related compounds; silicates; borates; stearates and other lubricants including MoS₂ and PbS; methyl cellulose and related compounds; organic liquids such as acetone, polyvinyl butyryl, polyvinyl alcohol, polyethylene glycol, oils of various kinds, tetraisoamyloxide, and The plasticizer may also be a colloidal liquid such as colloidal alumina, colloidal ceria, colloidal yttria, colloidal silica, colloidal zirconia, mono-aluminum phosphate, colloidal cerium acetate or mixtures thereof. Colloidal binders can also be derived from a suspension containing colloid precursors and reagents which are solutions of at least one salt such as chlorides, sulfates, nitrates, chlorates, perchlorates or metal organic compounds. Colloidal binders will usually be relatively dilute aqueous or non-aqueous suspensions, but the use of concentrated colloids or partly or fully precipitated colloids is also possible. Alternatively, the colloidal binder can be derived from a suspension containing chelating agents such as acetyl acetone and ethylacetoacetate. Various mixtures of different carriers are possible. When using colloids, three types of colloidal processing are possible. The first involves the gelation of certain polysaccharide solutions. The other two involve colloids and metal organic compounds. These last two involve the mixing of materials in a very fine scale. Colloids may be defined as comprising a dispersed phase with at least one dimension between 0.5 nm (nanometer) and about 10 microns (micrometers) in a dispersion medium which in the present case is a liquid. The magnitude of this dimension distinguishes colloids from bulk systems in the following (a) an extremely large surface area and (b) a significant percentage of molecules reside in the surface of colloidal systems. Up to 40% of molecules may reside on the surface. The colloidal systems which are important to this invention are both the thermodynamically stable lyophilic type (which include macro molecular systems such as polymers) and the kinetically stable lyophobic type (those that contain

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particles). In the formation of the slurry, new materials and other agents or diluents may be mixed in with the plasticizers.

- 3) One diluent may be a powder additive containing carbides, silicides, borides, aluminides, nitrides, oxides, carbonitrides, oxynitrides and combinations thereof. When choosing combinations of powder additives, the particle size selection is important. It is preferable to choose particle sizes below 100 microns and when employing combinations of powder additives, to choose particle sizes which are varied such that the packing of particles is optimized. Generally, the ratio of the particle sizes will be in the range from about 2:1 to about 5:1. Sometimes packing is optimized by choosing one constituent size three times smaller than the other constituent, i.e., having a particle ratio size of about 3:1.
- 4) Metallic particles, intermetallic particles or a combination thereof, for example Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, NiAl, NiAl₃, CrSi, CrB, etc. The sizes of these particles are also preferably varied to achieve optimum packing, like with the above powder additives.
- formula M(OR)_z, where M is a metal or a complex cation made up of two or more elements, R is an alkyl chain and z is a number usually in the range from 1 to 12. Alternatively, these metal alkoxides can be described as solutions in which molecules of organic groups are bound to a metal atom through oxygen. Examples of metal alkoxides are silicon tetraisoamyloxide, aluminum butoxide, aluminum isopropoxide, tetraethyl orthosilicates, etc. The organic portions of other metal organic compounds may include formates, acetates and acetylacetonates.
- 6) Pyrolizable chlorosilanes, polycarbosilanes, polysilazanes and other organosilicon polymers may be used as binders which pyrolize to useful products for oxidation prevention. Such compounds are expected to participate in the micropyretic reaction in a beneficial but complex manner to increase the yield of useful products with a morphology and size useful for the membrane. Organosilicon polymers

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typically dissolve in water and therefore should be avoided when producing membranes for filtering aqueous solutions.

- 7) Alkaline or acitic solutions may be needed to modify the pH of the slurry. Standard laboratory grade alkalines and acids are used.
 - 8) Burnable and/or oxidizable liquid or solid constituents such as polymers (e.g., polyurethane, polyester) or carbonaceous materials may be added to the slurry to be eventually burned off leaving behind a predetermined pore size and pore volume (density) in the membrane.

Tables V and VI give examples of typical slurry compositions.

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TABLE V

EXAMPLES OF MICROPYRETIC SLURRY COMPOSITIONS

SAMPLE	SOLID POWDER COMPOSITION (Wt %/Particle Size)	LIQUID CARRIER (Vol. %)	POWDER/ CARRIER (g/ml)
-	SiC (60%/3 Microns), Si ₃ N ₄ (10%/1 Micron), Ti (17%/-325 Mesh)*, and TiB ₂ (5%/-325 Mesh)*	Colloidal - Silica 50% Colloidal - Alumina 50%	10/6
2	SiC (72.5%/1-3 Microns), Si ₃ N ₄ (2.5%/0.1-1 Micron), Y ₂ O ₃ (5%/0.1-1 Micron), Ti (15%/-325 Mesh)*, and Si (5%/-325 Mesh)*	Colloidal-Silica 50% Colloidal-Alumina 50%	10/5
8	SiC (50%/1 Micron), Zr (4%/1 Micron), B (5%/1 Micron), C (7%/1 Micron), A1 (3%/-325 Mesh)*, Ti (27%/-325 Mesh)*, A1 ₂ 0 ₃ (2%/0.3 Microns), MoSi ₂ (0.5%/0.5 Microns), Cr ₂ 0 ₃ (0.5%/0.5 Microns), and TiB ₂ (1%/1 Micron)	"Colloidal Yttria, Polycarbosilane, Mono- aluminum phosphate, Methyl Cellulose, Polyvinyl Alcohol, Colloidal Ceria, Colloidal Zirconia	10/6

-325 mesh

44 microns

any of these liquid carriers may be used alone or in combination.

TABLE VI

EXAMPLES OF NON-MICROPYRETIC SLURRY COMPOSITIONS

	_	
LIQUID CARRIER (Vol. %)	Colloidal Alumina (10 ml)	Colloidal Alumina (10 ml)
SOLID POWDER COMPOSITION (Wt %/Particle Size)	TiB ₂ (25 gms / 1 Micron)	CrB ₂ (25 gms / 10 Microns)
SAMPLE	1	2

Once the desired slurry mixture is prepared, the slurry is then dried into a green form having a desired geometric configuration. The slurry may be applied to the surface of a substrate or article. The applied slurry is then dried, such as by air drying or being baked at relatively low temperatures, for example, in an oven, usually so as not to start the micropyretic reaction. There are various methods of applying the slurry including painting (by brush or roller), dipping, spraying, or pouring the liquid onto the surface. Typically, each coating of the slurry is allowed to dry before another coating is added. However, the underlying coating does not necessarily need to be entirely dry before the next coating is applied. If one or more coatings with micropyretic constituents are present, then it is preferable to dry these coatings completely prior to firing (i.e., the combustion step). Multiple coatings may be necessary in order to obtain the desired layer thickness. Depending upon the slurry composition, additional coatings may be added to already fired layers either for repair or for additional build up. Even when micropyretic constituents are absent, it is preferred to heat the green membrane with a suitable heat source, such as a torch (e.g., butane or oxyacetylene), a laser, a furnace, etc., if improvement in the densification of the membrane is required. Such heating takes place preferably in air but could be in other oxidizing atmospheres or in inert or reducing atmospheres.

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In general, the micropyretic layers provide heat for the bonding of several layers as well as bonding to the substrate or article. While membranes with multiple micropyretic layers can be produced according to the invention, multilayer membranes with one or more non-micropyretic layers can also be produced, if desired. These non-micropyretic layers could for example be made of polymers.

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If desired, bonding of the coatings to the surface of the substrate or article can be enhanced by treating the surface. The surface may be treated by sandblasting or pickling with acids or fluxes such as cryolite or other combinations of fluorides and chlorides prior to the application of the coating. Similarly, the substrate may be cleaned with an organic solvent such as acetone to remove oily products or other debris prior to the application of the coating.

In the case of micropyretic coatings, an additional step after the drying of the slurry coating(s) will be the firing or combustion of the slurry constituents (i.e., the membrane in its green state). Combustion of the green membrane can be performed by direct flame, concentrated sunlight, a plasma, a laser or an electron beam. In addition, if the substrate or article is conductive, the green form can be combusted by passing a current through the substrate or article. The coated substrate or article could also be placed inside a furnace at a predetermined temperature and time or heated by an induction method or by radiant heating. The applied slurry contains particulate substances which sinter above a given temperature, in particular reactant and/or non-reactant substances that reaction sinter at a temperature greater than about 0.5 Tm, where Tm is the melting point of the lowest melting reaction product.

Additional heat can be applied to a membrane in order to reduce the pore size and pore density in the membrane. The present method is good for obtaining membranes with pore sizes ranging from 10 nanometers to 100 microns. In-situ repair, rather than replacement of membranes by using the principles of the present invention is also contemplated.

Conductive Coating Application Process

Another aspect of the present invention concerns a process for applying a conductive coating wherein a slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof, is provided. The slurry may contain conventional amounts of suspension agents, surfactants and anti-foaming agents, e.g., in total up to about 5% by volume, in order to facilitate application, wetting and impregnation of the substrate.

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The concentration of ceramic precursors in the aqueous slurry is not critical and may be any amount which will obtain a viscosity such that wetting of the foamed polymer is ensured without excessive run-off. The type of foamed polymer (if used), is not critical, although it is preferred to select a thermoplastic or thermosetting polymer which will volatilize or decompose at a temperature not exceeding about 1100° C. In general, conventional foamed polymers which will volatilize, decompose or char when heated to a temperature of about 400° to about 1100° C. are suitable, such as polyurethane, polyvinyl chloride, polyethylene and polypropylene. Cellulose sponge and natural or polymeric fibers in woven or non-woven form may also be used and are intended to be included within the generic term foamed polymer.

The method of application of the slurry to the foamed polymer, i.e., impregnation, is what leads to the dramatic improvements afforded this aspect by the present invention over the process of the '737 patent. The impregnation is achieved by (a) fluidizing said slurry with steam or heated water and spraying the shape with said fluidized slurry or (b) heating said slurry so as to reduce its viscosity and spraying the shape with said reduced viscosity slurry.

The impregnation step of this aspect of the present invention obviates the dripping involved in the '737 process, thereby making the process less awkward and cumbersome. This also avoids the collapse of the "green structure" during processing, as observed in the '737 patent. Furthermore, the present method of impregnation avoids "distortion" of the formed article. Additionally, the steam or heated water or hot liquid constituent of the spray better dissolves certain constituents more easily, such as calcium silicates (cements) such as (CaO)₃.(SiO₂)₂.(H₂O)₃, which lead to a high green and final strength by precipitating out on the deposited surface.

The slurry-impregnated polymer is heated to a temperature of about 400° to about 1100° C, in order to drive off the polymer. The slurry-impregnated polymer may next again be dipped into the slurry after the heating step and dried. The dipping and drying may be done several times. If it is desired to obtain a *coated* porous

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ceramic, ceramic composite or metal structure, a preexisting ceramic, ceramic composite or metal body is impregnated with the slurry as described above.

Finally, the impregnated structure is ignited and/or heated by means of an electric arc, electric spark, flame, welding electrode, laser or in a furnace or by other conventional methods to initiate combustion synthesis and/or to sinter the impregnated structure. The final product is a conductive porous ceramic structure or a coated (the coating being conductive), porous ceramic, ceramic composite or metal structure. Thus, the products of the present invention may act both as filters and, due to their conductiveness, as heating elements. As stated above, because the heating element and filter are one and the same, less heat is lost due to radiation and the heat is available precisely where required, i.e. in the filter (which is also the heating element). It is also possible to incorporate in the conductive body, a "second" heating element which is a separate structure, which further improves the capability of the heating the filter. The "two-in-one" heating element-filter may also be fitted with a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise.

The ceramic precursors may comprise powder mixtures containing from about 35% to about 55% metallic aluminum, about 25% to about 35% titanium dioxide (titania), and about 20% to about 30% boric oxide, all percentages being by weight.

Another mixture of ceramic precursors in particulate form may comprise from about 65% to about 75% silicon and from about 25% to about 35% graphite, the percentages being by weight.

In another embodiment the ceramic precursors may comprise mixtures containing from about 20% to about 30% metallic aluminum, about 20% to about 25% titania, about 15% to about 25% boric oxide, about 25% to about 30% zirconium oxide, all percentages being by weight.

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The ceramic precursors may further comprise from about 20% to about 30% metallic aluminum, about 20% to about 25% titania, about 15% to about 25% boric oxide, and about 25% to about 35% powdered niobium, all percentages being by weight.

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Still another precursor mixture may comprise from about 20% to about 30% metallic aluminum, about 20% to about 25% titania, about 15% to about 25% boric oxide, about 20% to about 25% aluminum oxide, and about 3% to about 10% zirconium oxide, all percentages being by weight.

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Where a micropyretic reaction is involved, the particle size of the ceramic precursors is of importance in determining the rate of reaction propagation. For purposes of the present process, particle sizes ranging from about 1 to about 150 microns have been found to be preferable.

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It will be understood that the present process is not limited to any particular size or shape of ceramic structure, metal-ceramic composite structure or metallic structure, nor to the pore size thereof, as will be evident from the specific examples which follow. The atmosphere in which combustion synthesis is conducted is also not a limitation. In all embodiments described herein, combustion synthesis may be carried out in air at ambient pressure.

The ceramic, metal-ceramic or inter-metallic composite structure/coating is selected from the group consisting of borides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-titanium boride-titanium nitride; aluminum oxide-titanium boride-titanium oxide;

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molybdenum silicide-aluminum oxide; molybdenum boride-aluminum oxide; chromium carbide-aluminum oxide, vanadium nitride-aluminum oxide, aluminides of nickel, platinum-aluminum compounds, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite and mixtures thereof.

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In the following illustrative but non-limiting embodiments of this aspect of the invention, Examples 1 through 3 relate to the preparation of coatings having micropyretic constituents, while Examples 4 and 5 relate to coatings having non-micropyretic constituents.

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Aqueous slurries were prepared for the following mixtures. All constituents were powders and all percentages are in weight percent.

EXAMPLE 1

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55%Ni + 23%Al + 3%C + 10%SiO₂ + 2%Pt (catalyst powder form) + 2%CaCO₃ + 5%clay (the clay is selected from the montmorillonite group of clays, a group containing bentonite, sauconite, nontronite, saponite, hectonite and vermaculate, called three-layered clays) + water (10ml/50g powder)

20 EXAMPLE 2

57%MoO₃ + 21%Al + 22%Si + (diluents) + (catalysts such as Pt) (eg MoSi₂ or SiC)

+ colloidal silica(1ml/5g) + water (20ml/50g powder)

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EXAMPLE 3

60%Ti + 15%Si + 5%P + 10%Ni + 5%(SiC fibers) + 3%PtO₂ (powder) + 2%RuCl₂ (liquid) + colloidal silica + colloidal alumina + colloidal zirconia (approx 10ml/50g)

EXAMPLE 4

 $30\% Al_2O_3 + 25\% SiO_2 + 29\% ZrO_2 + 10\% (Al_2O_3 fibers) + 2\% RuCl_2 (ruthenium chloride) + 3\% PtO_2 (catalyst) + colloidal silica (10ml/15g) + 0.5\% TiO_2 + 0.5\% MgO$

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In some cases RuCl₂ was added later and heated to 430°C.

EXAMPLE 5

50% constituents of example 3 and 50% constituents of Example 4

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General Procedure

The slurries were fluidized and were well mixed in stainless steel containers. A spray machine/steam generator/portable oil fired steam cleaner (model 5Z170 made by Dayton Company) is used to generate a spray of hot liquid or steam or water. It is a 66 gallon per hour machine which operates at up to 180 psi. Generally, the hot liquid or steam or water is sprayed on the slurry with a nozzle at a pressure of 10ppi. A polymeric foam cylinder approximately 3" diameter and 4" height was used. Uniform coating of the foam stems was obtained and the pressure of the jet helped to keep the pores open. After each spray a 5 minute drying time was allowed before the next layer was deposited. The layers were allowed to build up until a 0.35 mm stem thickness was obtained. The non-distorted mass was then heated to 350°C to drive away the polymer and a green ceramic or ceramic composite structure was obtained. The mass was then placed in a furnace. Furnace temperature for examples 1-3 was 1150°C, for examples 4 and 5, it was 1600°C. In all cases, either through micropyretic sintering, or conventional sintering a solid ceramic porous body was obtained. Examples 1 through 3 produced conductive coatings whereas 4 and 5 were not conductive.

While specific examples of coating porous ceramic, ceramic composite or metal structures have not been provided, the slurries described above are equally applicable for producing coated articles and the advantages afforded by the

impregnation method of the present invention extend to manufacture of coated articles as well.

From the above disclosure of the general principles of the present invention and the preceding detailed description, those skilled in the art will readily comprehend the various modifications to which the present invention is susceptible. Therefore, the scope of the invention should be limited only by the following claims and equivalents thereof.

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vanadium; carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, iron, molybdenum, vanadium and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-titanium boride-titanium nitride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum silicide-aluminum oxide; molybdenum boride-aluminum oxide; chromium carbide-aluminum oxide; vanadium nitride-aluminum oxide, aluminides of nickel, platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

- 9. The modulated filter of claim 1, wherein the pores in said composite are approximately 10-80 pores per inch.
- 10. The modulated filter of claim 8, wherein each said composite further comprises metallic particles, intermetallic particles and compounds and combinations thereof.
- 11. The modulated filter of claim 10, wherein said metallic particles, intermetallic particles or combinations thereof are selected from the group consisting of Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, Rh, Ru, NiAl, NiAl₃, CrSi, CrB Ti₅Si₃, NbB, Nb₃Al, NbAl₃, Nb₂Al and compounds and mixtures thereof.
 - 12. A regenerative filter comprising:

 a means for filtering including at least one porous ceramic,
 metal-ceramic or inter-metallic composite having been
 manufactured using micropyretic synthesis; and

a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means.

- 13. The regenerative filter of claim 12, wherein said regenerating means is formed in situ with said filtering means.
- 14. The regenerative filter of claim 12, wherein said composite is reticulated.
- 15. The regenerative filter of claim 12, wherein the means for regenerating comprises a catalyst.
- 16. The regenerative filter of claim 15, wherein the catalyst is applied to the filter by a method selected from the group consisting of coating, impregnating, and combinations thereof.
- 17. The regenerative filter of claim 15, wherein the catalyst can react or be reactive under conditions of vacuum, room temperature, increased temperature, pressure or combinations thereof.
- 18. The regenerative filter of claim 12, wherein said means for regenerating comprises a heating element.
- 19. The regenerative filter of claim 18, wherein said heating element is formed in situ with said filtering means.
- 20. The regenerative filter of claim 18, wherein said heating element comprises a compound selected from the group consisting of metallic material, molysilicides, Fe-Cr-Al, Ni-Cr, SiC and compounds and combinations thereof.
- 21. The regenerative filter of claim 18, wherein said heating element comprises a material selected from the group consisting of borides or aluminides of

titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum silicide-aluminum oxide; molybdenum silicide-aluminum oxide; molybdenum silicide-aluminum oxide; of nickel, platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

- 22. The regenerative filter of claim 21, wherein each said composite further comprises metallic particles, intermetallic particles or compounds or combinations thereof.
- 23. The regenerative filter of claim 22, wherein said metallic particles, intermetallic particles or combinations thereof are selected from the group consisting of Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, Rh, Ru, NiAl, NiAl₃, CrSi, CrB Ti₅Si₃, NbB, Nb₃Al, NbAl₃, Nb₂Al and compounds and mixtures thereof.
- 24. The regenerative filter of claims 18, 19, 20, or 21 wherein said heating element is a high resistivity heating element, with a resistivity of between around 50-5000 μ ohm-cm.
- 25. In a land-based vehicle, water-based vehicle, in power generation equipment or in an industrial engine, said vehicles, equipment or engine including a body and an exhaust system, the improvement comprising: a modulated filter for gaseous, liquid and particulate matter, wherein the modules in said filter are porous

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ceramic, metal-ceramic or inter-metallic composites, said structures having been manufactured using micropyretic synthesis, the filter including at least two porous ceramic, metal-ceramic or inter-metallic composites.

- 26. The improvement of claim 25, wherein the filter includes a catalyst.
- 27. The improvement of claim 26, wherein the catalyst is applied to the filter by a method selected from the group consisting of coating, impregnating, and combinations thereof.
- 28. The improvement of claim 26, wherein the catalyst can react or be reactive under conditions of vacuum, room temperature, increased temperature, pressure or combinations thereof.
- 29. The improvement of claim 26, wherein each said module is optimized for extracting different materials.
- 30. The improvement of claim 29, wherein said materials are selected from the group consisting of particulates, carbon particles, NO_x , CO, CO_2 , SO_2 , hydrocarbons, and combinations thereof.
- 31. The improvement of claim 25, wherein said composites have rough surfaces, said roughness being enhanced chemically or mechanically.
 - 32. The improvement of claim 25, wherein said composites are reticulated.
- 33. The improvement of claim 25, wherein each said composite comprises a material selected from the group consisting of borides or aluminides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, iron, molybdenum, vanadium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium,

boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-titanium boride-titanium nitride; aluminum oxide-titanium boride-titanium oxide; molybdenum silicide-aluminum oxide; molybdenum silicide-aluminum oxide; chromium carbide-aluminum oxide; vanadium nitride-aluminum oxide, aluminides of nickel, platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

- 34. The improvement of claim 33, further comprising metallic particles, intermetallic particles and compounds and combinations thereof.
- 35. The improvement of claim 34, wherein said metallic particles, intermetallic particles or combinations thereof are selected from the group consisting of Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, Rh, Ru, NiAl, NiAl₃, CrSi, CrB Ti₅Si₃, NbB, Nb₃Al, NbAl₃, Nb₂Al and compounds and mixtures thereof.
- 36. The improvement of claim 25, wherein the pores in said composite are 10-80 pores per inch.
- 37. In a land-based vehicle, water-based vehicle, in power generation equipment or in an industrial engine, said vehicles, equipment or engine, including a body and an exhaust system, the improvement comprising: a regenerative filter in the exhaust system including a means for filtering which comprises at least one porous ceramic, metal-ceramic or inter-metallic composite having been manufactured using micropyretic synthesis and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means.

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38. The improvement of claim 37, wherein said regenerating means is formed in situ with said filtering means.

- 39. The improvement of claim 37, wherein said ceramic, metal-ceramic or inter-metallic composite is reticulated.
- 40. The improvement of claim 37, wherein said means for regenerating comprises a heating element.
- 41. The improvement of claim 37, wherein said means for filtering comprises reticulated ceramic, metal-ceramic or inter-metallic composites having been manufactured using micropyretic synthesis; and said means for regenerating comprises a heating element.
- 42. The improvement of claim 41, wherein said heating element is formed in situ with said filtering element.
- 43. The improvement of claim 42, wherein said heating element comprises a compound selected from the group consisting of metallic material, molysilicides, Fe-Cr-Al, Ni-Cr, SiC and combinations thereof.
- 44. The improvement of claim 40, wherein said heating element comprises a material selected from the group consisting of borides or aluminides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride-titanium oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum silicide-aluminum oxide; molybdenum

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boride-aluminum oxide; chromium carbide-aluminum oxide, vanadium nitride-aluminum oxide, aluminides of nickel, platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof in the form of coatings phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

- 45. The improvement of claim 44, further comprising metallic particles, intermetallic particles and compounds and combinations thereof.
- 46. The improvement of claim 45, wherein said metallic particles, intermetallic particles or combinations thereof are selected from the group consisting of Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, Rh, Ru, NiAl, NiAl₃, CrSi, CrB Ti₅Si₃, NbB, Nb₃Al, NbAl₃, Nb₂Al and compounds and mixtures thereof.
- 47. The improvement of claims 40, 41, 42, or 43 wherein said heating element is a high resistivity heating element, with a resistivity of between around 50-5000 μ ohm-cm.
 - 48. In a regenerative exhaust system, the improvement comprising:
 a modulated filter for gaseous, liquid and particulate matter, wherein
 the modules in said filter are porous ceramic, metal-ceramic or intermetallic composites, said composites having been manufactured using
 micropyretic synthesis, the filter including at least two modules.
 - 49. The improvement of claim 48, wherein the filter includes a catalyst.
- 50. The improvement of claim 49, wherein the catalyst is applied to the filter by a method selected from the group consisting of coating, impregnating, application of a liquid, application of a gas, application of a pliable solid, and combinations thereof.

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51. The improvement of claim 49 wherein the catalyst can react or be reactive under conditions of vacuum, room temperature, increased temperature, pressure or combinations thereof.

- 52. The improvement of claim 48, wherein each said module is optimized for extracting different materials.
- 53. The improvement of claim 52, wherein said materials are selected from the group consisting of particulates, carbon particles, NO_x, CO, CO₂, SO₂, hydrocarbons, and combinations thereof.
- 54. The improvement of claim 50, wherein said porous composites have rough surfaces, said roughness being enhanced chemically or mechanically.
 - 55. The improvement of claim 48, wherein said composites are reticulated.
- **5**6. The improvement of claim 48, wherein each said composites comprises a material selected from the group consisting of borides or aluminides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, iron, molybdenum, vanadium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-titanium boride-titanium nitride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum, silicidealuminum oxide; molybdenum boride-aluminum oxide; chromium carbide-aluminum oxide; vanadium nitride-aluminum oxide, aluminides of nickel, platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of

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ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

- 57. The improvement of claim 56, further comprising metallic particles, intermetallic particles and compounds and combinations thereof.
- 58. The improvement of claim 57, wherein said particles, intermetallic particles or combinations thereof are selected from the group consisting of Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, Rh, Ru, NiAl, NiAl₃, CrSi, CrB Ti₅Si₃, NbB, Nb₃Al, NbAl₃, Nb₂Al and compounds and mixtures thereof.
- 59. The improvement of claim 48, wherein the pores in said composites are 10-80 pores per inch.
 - 60. In a regenerative exhaust system, the improvement comprising: a regenerative filter comprising a means for filtering which comprises a porous ceramic, metal-ceramic or inter-metallic composite having been manufactured using micropyretic synthesis, and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means.
- 61. The improvement of claim 60, wherein said regenerating means is formed in situ with said filtering means.
- 62. The improvement of claim 60, wherein said ceramic, metal-ceramic or inter-metallic composite is reticulated.
- 63. The improvement of claim 60, wherein said means for regenerating comprises a heating element.
- 64. The improvement of claim 63, wherein said heating element is formed in situ with said filtering means.

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- 65. The improvement of claim 64, wherein said heating element comprises a compound selected from the group consisting of metallic material, molysilicides, Fe-Cr-Al, Ni-Cr, SiC and combinations thereof.
- 66. The improvement of claim 63, wherein said heating element comprises a material selected from the group consisting of borides or aluminides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxidetitanium boride-titanium nitride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum silicide-aluminum oxide; molybdenum boride-aluminum oxide; chromium carbide-aluminum oxide, vanadium nitridealuminum oxide, aluminides of nickel, platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.
- 67. The improvement of claim 66, wherein said composite further comprises metallic particles, intermetallic particles and compounds and combinations thereof.
- 68. The improvement of claim 67, wherein said particles, intermetallic particles or combinations thereof are selected from the group consisting of Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, Rh, Ru, NiAl, NiAl₃, CrSi, CrB Ti₅Si₃, NbB, Nb₃Al, NbAl₃, Nb₂Al and compounds and mixtures thereof.

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- 69. The improvement of claims 63, 64, 65, or 66, wherein said heating element is a high resistivity heating element, with a resistivity of between around 50-5000 μ ohm-cm.
- 70. In a catalytic converter including a catalyst, the improvement comprising: a modulated filter for gaseous, liquid and particulate matter, wherein each of the modules in said filter is a porous ceramic, metal-ceramic or inter-metallic composite, said having been manufactured using micropyretic synthesis, the filter including at least two modules.
- 71. The improvement of claim 70, wherein the catalyst is applied to the filter by a method selected from the group consisting of coating, impregnating, and combinations thereof.
- 72. The improvement of claim 70, wherein the catalyst can react or be reactive under conditions of vacuum, room temperature, increased temperature, pressure or combinations thereof.
- 73. The improvement of claim 70, wherein each said module is optimized for extracting different materials.
- 74. The improvement of claim 70, wherein said materials are selected from the group consisting of particulates, carbon particles, NO_x, CO, CO₂, SO₂, hydrocarbons, and combinations thereof.
- 75. The improvement of claim 70, wherein said composites have rough surfaces, said roughness being enhanced chemically or mechanically.
 - 76. The improvement of claim 69, wherein said composites are reticulated.
- 77. The improvement of claim 69, wherein the composite comprises a material selected from the group consisting of borides or aluminides of titanium,

zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides and oxides of titanium, hafnium, boron, aluminum, tantalum, silicon, 5 tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-10 titanium boride-titanium nitride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum, silicide-aluminum oxide; molybdenum boride-aluminum oxide; chromium carbide-aluminum oxide, vanadium nitridealuminum oxide, aluminides of nickel, platinum, ruthenium, rhodium, gold, silver, iron, titanium and palladium and compounds thereof in the form of coatings, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, 15 cordierite, lanthanum chromite, graphite and compounds and mixtures thereof.

- 78. The improvement of claim 77, wherein said composite further comprises metallic particles, intermetallic particles and compounds and combinations thereof.
- 79. The improvement of claim 78, wherein said metallic particles, intermetallic particles or combinations thereof are selected from the group consisting of Cu, Ni, Pt, Al, Cr, Zr, Zn, Mg, Fe, Mn, Rh, Ru, NiAl, NiAl₃, CrSi, CrB Ti₅Si₃, NbB, Nb₃Al, NbAl₃, Nb₂Al and compounds and mixtures thereof.
- 80. The improvement of claim 70, wherein the pores in said composites are 10-80 pores per inch.
- 81. A modulated regenerative filter for gaseous, liquid and particulate matter, wherein the modules in said filter are porous ceramic, metal-ceramic or intermetallic composites, said structures having been manufactured using micropyretic synthesis, the filter comprising:
 - at least two porous ceramic or ceramic composite structures; and

a means for regenerating said filter, said means for regenerating being integral with said structures.

- 82. In a land-based vehicle, water-based vehicle, in power generation equipment or in an industrial engine, said vehicles, equipment or engine, including a body and an exhaust system, the improvement comprising: a means for heating selected from the group consisting of a high resistivity heating element, a heating element having high emissivity, a heating element having both high resistivity and high emissivity, an ignitor, a laser, a spark producing means, a means for inducing a chemical reaction and combinations thereof.
- 83. In a land-based vehicle, water-based vehicle, in power generation equipment or in an industrial engine, said vehicles, equipment or engine, including a body and an exhaust system, the improvement comprising: a regenerative filter in the exhaust system comprising a means for filtering which includes at least one porous ceramic, metal-ceramic or inter-metallic composite manufactured using micropyretic synthesis and a heating element having high resistivity, or having high emissivity or having both high resistivity and emissivity, for regenerating said means for filtering.
- 84. A land-based vehicle, water-based vehicle, power generation equipment or an industrial engine which causes the emission of exhaust gases including particulates, in combination with the filter of claim 1 or claim 13, said vehicles, equipment or engine including a diesel engine and means for preheating the exhaust gases prior to the gases entering said filter, said means for preheating including a high resistivity heating element, or a high emissivity heating element, or a heating element having both high resistivity and high emissivity.
- 85. A land-based vehicle, water-based vehicle, power generation equipment or an industrial engine which causes the emission of exhaust gases including particulates, in combination with the filter of claim 1, 12 or 15, whereby heated fluids

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are released from said filter, said vehicles, equipment or engine being adapted to utilize the heat from said fluids elsewhere in vehicles, equipment or engine.

- 86. The filter of claims 1, 12, or 15, wherein said composites are in the form of porous membranes.
- 87. A land based vehicle, water-based vehicle, power generation equipment or an industrial engine which causes the emission of exhaust gases including in combination with the filter of claims 1, 12 or 15, a device selected from the group consisting of an ignitor, a spark producing means, a heating element, a laser means, a means for inducing a chemical reaction, electrochemical reaction means, electrospark producing means, electrostatic separation means and combinations thereof.
- 88. The filter of claim 87, wherein at least two of the listed devices are present.
- 89. The filter of claim 87, wherein said devices cause the combustion of said particulates and of said exhaust gases.
- 90. The filter of claim 87, wherein said device is a spark providing means which causes intermittent or pulsed sparks or discharges so as to cause the combustion of said particulates and exhaust gases.
- 91. The filter of claims 82 or 87 wherein a surface is not required for combustion of said particulates or exhaust gases into innocuous gases.
- 92. The filters of claims 1, 12, or 15, wherein said filter is capable of attaining an operative temperature of up to 1200°C.
- 93. The filter of claim 15, further comprising a means for gauging the aging of the catalyst.

- 94. The filter of claim 12, wherein said means for regenerating comprises a heating element and an electrical terminal.
- 95. The filter of claim 94, wherein said heating element and electrical terminal and formed of the same material.
- 96. The filter of claim 12, wherein said means for regenerating comprises a plurality of heating elements in combination with a ballast.
- 97. The filter of claim 12, wherein said means for regenerating is a thin film resistor.
- 98. The filter of claim 12, wherein said means for regenerating comprises a device which acts as a solid state switch.
- 99. The filter of claim 98, wherein said device is formed of a piezo electric substance.
- 100. The filter of claim 99, wherein said piezo electric substance is a spinel ferrite.
- 101. The filter of claim 100, wherein said ferrite is barium or strontium titanate or mixtures thereof.
 - 102. The filter of claim 101, wherein said titanates are doped.
- 103. The filter of claim 98, wherein said means for regenerating further comprises a heating element.
- 104. The filter of claim 99, wherein said device is formed of an electro-optic ceramic substance.

105. The filter of claim 98, wherein said device is formed of a substance having a positive temperature coefficient.

- 106. The filter of claim 12, wherein said means for regenerating comprises a device selected from the group consisting of thyristors, varistors or combinations thereof.
- 107. Use of the filter of claim 86, in furnaces used in producing wax and like substances.
- 108. The filter of claim 85 being specially adapted for receiving external combustible matter for combustion, so as to generate additional heat.
- 109. The filter of claim 108, wherein said combustible matter is selected from the group consisting of carbon, gasoline products, hydrocarbons, solid fuels, metals or any matter which reacts with a positive enthalpy change.
- 110. In a process for producing a porous ceramic or ceramic composite structure, comprising the steps of providing a slurry comprising ceramic precursors, impregnating a foamed polymer shape with said slurry, heating the slurry-impregnated polymer shape to a temperature sufficient to remove said polymer, and heating said ceramic precursors to obtain a ceramic or ceramic composite structure porosity an improvement process for producing a coated porous ceramic, ceramic composite or metal structure, the improvement process comprising the steps of:

providing a slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof;

impregnating a ceramic, ceramic composite or metal shape with said slurry by (a) fluidizing said slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry; and

obtaining a coated porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or by heating said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material so as to cause said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material to adhere to said porous ceramic, ceramic composite or metal structure.

- 111. The improvement process of claim 110, wherein said shape is selected from the group consisting of fibers, reticulated and non-reticulated foam structures, straight-through ceramic channel structure and porous and non-porous metallic structures.
- 112. The improvement process of claim 111, wherein said slurry contains at least one of suspension agents, binders, surfactants and anti-foaming agents.
- 113. In a process for producing a porous ceramic or ceramic composite structure, comprising the steps of providing a slurry comprising ceramic precursors capable of undergoing combustion synthesis, impregnating a foamed polymer shape with said slurry, heating the slurry-impregnated polymer shape to a temperature sufficient to remove said polymer, and igniting said ceramic precursors to initiate combustion synthesis, thereby obtaining a ceramic or ceramic composite structure having interconnected porosity and controlled pore size, an improvement process for producing a porous ceramic or ceramic composite, the improvement process comprising the steps of:

providing an improved slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate.

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ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof; impregnating said polymeric shape with said improved slurry by (a) fluidizing said improved slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said improved slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry; heating the improved-slurry-impregnated polymer shape to a temperature sufficient to remove said polymer; and obtaining a porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or

by heating said non-micropyretic particulate ceramic, metal, intermetallic or polymeric material so as to cause said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material.

- 114. The process of claim 113, wherein said improved-slurry-impregnated polymer shape is heated to a temperature of about 400° to about 1100° C. in order to volatilize or decompose said polymer.
- 115. The process of claim 113, including the step of applying a second improved slurry to said improved-slurry-impregnated polymer shape, said second slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof.

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- 116. The process of claim 110 or 113, wherein said ceramic or ceramic composite structure/coating comprises a material selected from the group consisting of borides of titanium, zirconium, niobium, tantalum, molybdenum, hafnium, chromium, and vanadium; carbides of titanium, hafnium, boron, aluminum, tantalum, silicon, tungsten, zirconium, niobium, and chromium; carbonitrides of titanium, niobium, and tantalum; nitrides of titanium, zirconium, boron, aluminum, silicon, tantalum, hafnium, and niobium; silicides of molybdenum, titanium, zirconium, niobium, tantalum, tungsten and vanadium; hydrides of titanium, zirconium and niobium; aluminum oxide-titanium boride; titanium carbide-titanium boride; aluminum oxide-titanium boride-titanium carbide; boron carbide-aluminum oxide; molybdenum silicide-aluminum oxide; molybdenum silicide-aluminum oxide, aluminides of nickel, platinum-aluminum compounds, phosphides of nickel, titanium-nickel, oxides and oxychlorides of ruthenium, mullite, cordierite and mixtures thereof.
 - 117. The process of claim 110 or 113, wherein said metal-ceramic composite is chosen from the group consisting of iron-aluminum oxide; aluminum-aluminum oxide-titanium boride; and titanium-titanium boride.
 - 118. The process of claim 110 or 117, wherein said ceramic precursors comprise a mixture of from about 65% to about 95% by weight titanium and about 5% to about 35% by weight boron, said titanium and boron having average particle sizes ranging from about 1 to about 150 microns.
 - 119. The process of claim 118, wherein said porous ceramic structure is a filter for molten metal, and wherein said ceramic precursors include additives for grain refining of said metal.
 - 120. The process of claim 110, wherein said ceramic precursors comprise a mixture of iron oxide and metallic aluminum in approximately stoichiometric

proportions and having average particle sizes ranging from about 1 to about 150 microns.

- 121. The process of claim 110 or 113, wherein said ceramic precursors comprise a mixture of about 35% to about 55% by weight aluminum, about 25% to about 35% by weight titanium dioxide, and about 20% to about 30% by weight boric oxide.
- 122. The process of claim 110 or 116, wherein said ceramic precursors comprise a mixture of from about 65% to about 75% by weight silicon and from about 25% to about 35% by weight graphite.
- 123. The process of claim 110 or 113, wherein said ceramic precursors comprise a mixture of from about 20% to about 30% aluminum, about 20% to about 25% titanium dioxide, about 15% to about 25% boric oxide, and about 25% to about 35% zirconium oxide, all percentages being by weight.
- 124. The process of claim 110 or 113, wherein said ceramic precursors comprise a mixture of from about 20% to about 30% aluminum, about 20% to about 25% titanium dioxide, about 15% to about 25% boric oxide, and about 25% to about 35% powdered niobium, all percentages being by weight.
- 125. The process of claim 110 or 115, wherein said ceramic precursors comprise a mixture of from about 20% to about 30% aluminum, about 20% to about 25% titanium dioxide, about 15% to about 25% boric oxide, about 20% to about 25% aluminum oxide, and about 3% to about 10% zirconium oxide, all percentages being by weight.
- 126. A porous body which is itself conductive or to which is applied a conductive coating, which porous body can function as a heating element, so as to cause it to heat up if a current is applied through said body, and which can also

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function as a filter due to its porosity, wherein the heating element function and the filter function is accomplished by a single undivided structure.

127. The porous body of claim 126, wherein said body is itself conductive, said body being manufactured by a process comprising the steps of:

providing an improved slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof; impregnating said polymeric shape with said improved slurry by (a)

fluidizing said improved slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said improved slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry;

heating the improved-slurry-impregnated polymer shape to a temperature sufficient to remove said polymer; and obtaining a porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or by heating said non-micropyretic particulate ceramic, metal, intermetallic or polymeric material so as to cause said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material.

128. The porous body of claim 126, wherein a conductive coating is applied to said body, said body being a ceramic, ceramic composite or metal structure, the ceramic coating being applied by a process comprising the steps of:

providing a slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one

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polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof;

impregnating a ceramic, ceramic composite or metal shape with said slurry by (a) fluidizing said slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry; and

obtaining a coated porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or by heating said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material so as to cause said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material to adhere to said porous ceramic, ceramic composite or metal structure.

- 129. A heating element in close contact with a porous body which is itself conductive or to which is applied a conductive coating, which porous body can itself function as a heating element, so as to cause it to heat up if a current is applied through said body and which can also function as a filter due to its porosity, wherein the heating element function and the filter function of the porous body is accomplished by a single undivided structure.
- 130. The combination heating element porous body of claim 129, wherein said body itself is conductive, said body being manufactured by a process comprising the steps of:

providing an improved slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic

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materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof; impregnating said polymeric shape with said improved slurry by (a) fluidizing said improved slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said improved slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry;

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heating the improved-slurry-impregnated polymer shape to temperature sufficient to remove said polymer; and

obtaining a porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or by heating said non-micropyretic particulate ceramic, metal, intermetallic or polymeric material so as to cause said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material.

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131. The combination heating element-porous body of claim 129, wherein a conductive coating is applied to said body, said body being a ceramic, ceramic composite or metal structure, the coating being applied to said body by a process comprising the steps of:

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providing a slurry comprising (A) at least one component selected from the group consisting of (a) at least two particulate ceramic precursors capable of undergoing combustion synthesis, (b) at least one non-micropyretic particulate ceramic, (c) at least one metal, (d) at least one inter-metallic, (e) at least one polymeric material, and mixtures thereof; and (B) hydroplastic materials selected from the group consisting of clays, colloidal silica, colloidal alumina, colloidal zirconia, colloidal ceria and mixtures thereof;

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impregnating a ceramic, ceramic composite or metal shape with said slurry by (a) fluidizing said slurry with steam or heated water and spraying said shape with said fluidized slurry or (b) heating said slurry so as to reduce its viscosity and spraying said shape with said reduced viscosity slurry; and

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obtaining a coated porous ceramic, ceramic composite or metal structure by igniting said ceramic precursors to initiate combustion synthesis and/or by heating said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material so as to cause said non-micropyretic particulate ceramic, metal, inter-metallic or polymeric material to adhere to said porous ceramic, ceramic composite or metal structure.

- 132. A combination heating element-porous body as in claim 126, which comprises a second heating element, different in its composition from the first heating element.
- 133. A combination heating element-porous body as in claim 126, further comprising a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise.
- 134. In a regenerative filter comprising a means for filtering; and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means, the improvement comprising a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise.
- 135. A non-regenerative filter means in combination with a pressure release safety valve for removing collected particulate matter, the valve being self-resetting or otherwise.
- 136. The filter of claim 134 or 135, further including a means for heating the fluid entering the valve.
- 137. In a modulated filter for gaseous, liquid and particulate matter, wherein the modules in said filter are porous ceramic or ceramic composite structures, said structures having interconnected porosity and having been manufactured using micropyretic synthesis, the filter comprising at least two porous ceramic or ceramic

composite modules, the improvement including flexible flaps in between or after the modules, said flaps being made of materials selected from the group consisting of fiber cloth, high temperature wool and flexible boards, said flaps being susceptible to adherence by particulate fines.

- 138. The improvement of claim 137, wherein said flaps are flexible enough so that they are displaced if the flow rate of the fluid to be filtered increases beyond a specified value, but which flaps remove fine particulates at lower flow rates.
- 139. In a regenerative filter comprising a means for filtering; and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means, the improvement comprising fins, metallic fins, or other conductive fins inside the regenerative filter, said fins being used to better distribute heat within the regenerative filter.
- 140. In a modulated filter for gaseous, liquid and particulate matter, wherein the modules in said filter are porous ceramic or ceramic composite structures, said structures having interconnected porosity and having been manufactured using micropyretic synthesis, the filter comprising at least two porous ceramic or ceramic composite modules, the improvement comprising fins, metallic fins, or other conductive fins inside the regenerative filter, said fins being used to better distribute heat within the regenerative filter.
- 141. The filter of claims 1, 12 or 15, further comprising an energy storage device.
 - 142. The filter of claim 141, wherein said device is an inductor or a capacitor.
- 15 143. A separator for separating particles with different densities, comprising:
 a means for separating; and
 a heating element integrally connected to said means for separating.

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144. The separator of claim 143, wherein said separator as a vortex or a venturi tube.

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145. The means for separating of claim 144, wherein said separator is micropyretically synthesized.

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Fig. la

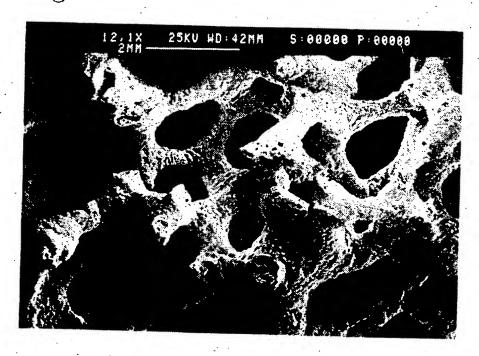
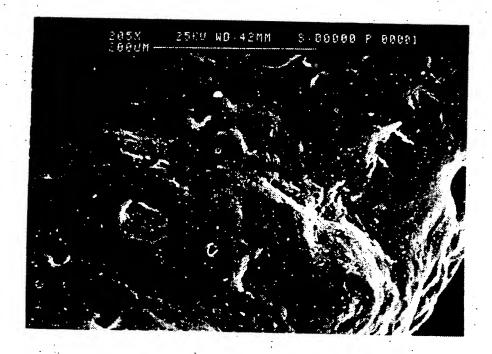


Fig. 1b



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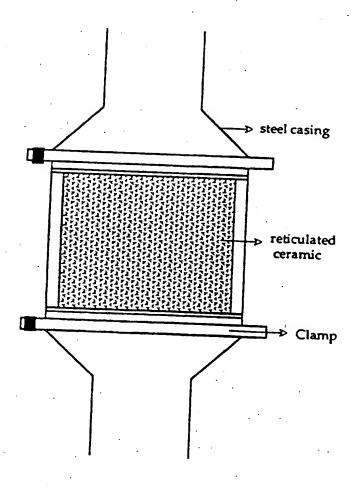
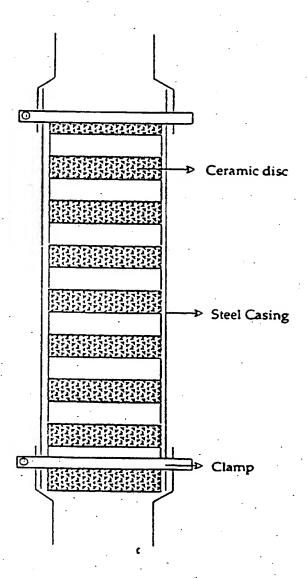
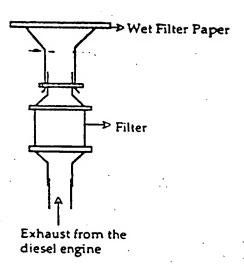


Figure 2



. Figure 3



Pigure 4

Fig. 5

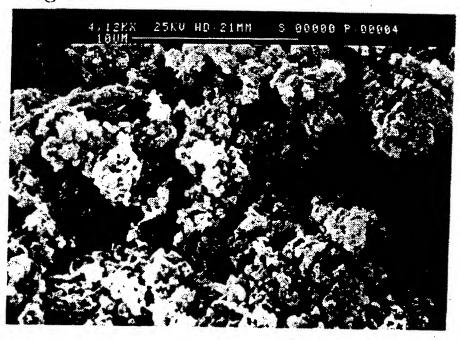
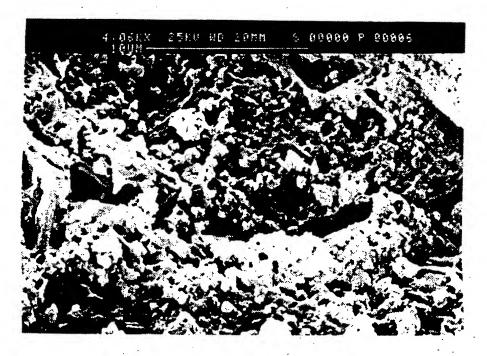


Fig. 6



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Fig. 7.

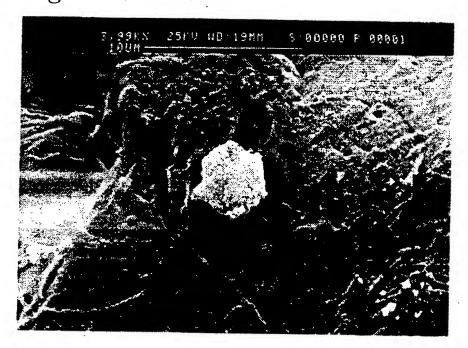


Fig. 8

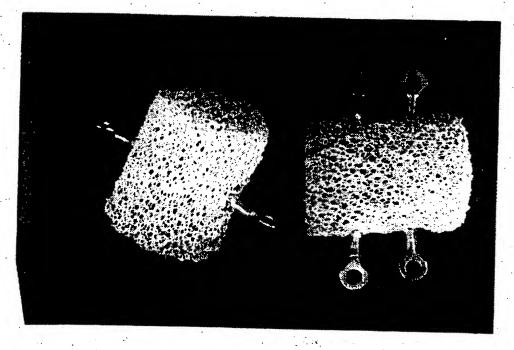
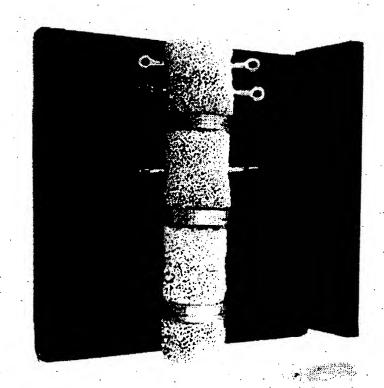


Fig. 9



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Fig. 10

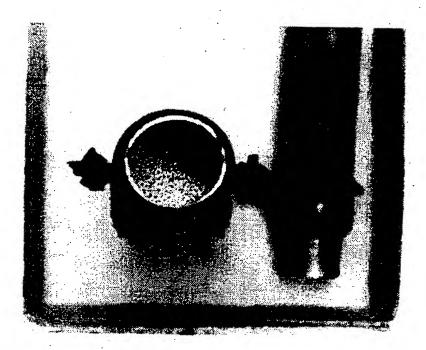
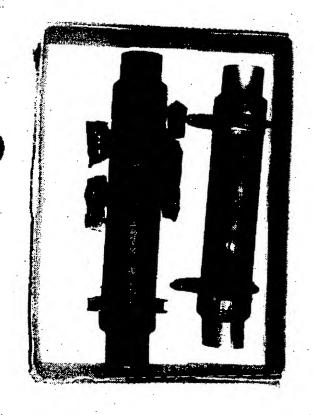


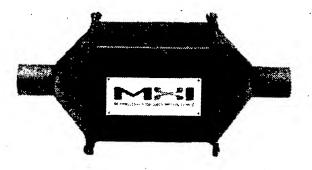
Fig. 11



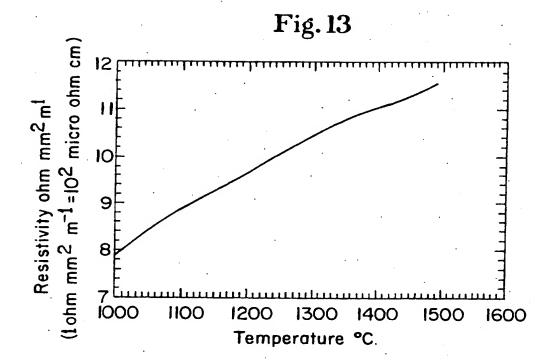
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Fig.12



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(88) Date of publication of the international search report: 21 March 1996 (21.03.96)

(54) Title: FILTER MANUFACTURED BY MICROPYRECTIC SYNTHESIS

(57) Abstract

A modular filter for gases liquid and particulate matter is disclosed, the filter comprising at least two porous ceramic or ceramic modules. A regenerative filter is also disclosed comprising a means for filtering; and a means for regenerating said means for filtering, said means for regenerating being integral with said filtering means. A method for coating articles with a conductive coating is also included. Devices which may be used in conjunction with both modular and/or regenerative filters are disclosed.

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A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C04B35/65 C22C1/05

F01N3/24

B01D53/74

CO4B38/00 B01D53/88

F01N1/02 B01D46/12 F01N3/10 B01D39/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 6 CO4B C22C FO1N BO1D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 279 737 (UNIVERSITY OF CINCINNATI) 18 January 1994	12-81, 83-125, 137,138, 140
	see column 1, line 12 - line 25 see column 4, line 18 - column 7, line 68; claims 1-19	
Α	DE,A,41 30 630 (FORSCHUNGSZENTRUM JÜLICH GMBH) 18 March 1993	12-81, 83-125, 137,138,
÷· ·	see column 1, line 42 - column 3, line 33; claims 1-9; figure 1	
	-/	3
		• .

X Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
"Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance. "E" earlier document but published on or after the international filling date. "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified). "O" document referring to an oral disclosure, use, exhibition or other means. "P" document published prior to the international filling date but later than the priority date claimed.	T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention. "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone. "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search 23 November 1995	Date of mailing of the international search report 1 9 -92- :
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tr. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer EIJKENBOOM, T

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PCT/US 95/06387

		PC1/05 9:	
C.(Continue Category *	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
A	EP,A,O 154 145 (DEGUSSA AG) 11 September 1985		12-81, 83-125, 137,138, 140
·	see page 5, line 22 - page 9, line 26; claims 1-7; figure 1		
4	EP,A,O 336 883 (STOBBE) 11 October 1989	·	12-81, 83-125, 137,138, 140
	see column 9, line 49 - column 10, line 45; claims 1-14; figures 1-8; examples 1-3		
\	EP,A,O 463 437 (BAYER AG) 2 January 1992	·	12-81, 83-125, 137,138, 140
	see page 3, line 7 - page 4, line 41; claims 1-14		
	EP,A,O 440 569 (PECHINEY ELECTROMETALLURGIE) 7 August 1991		12-81, 83-125, 137,138, 140
	see column 1, line 16 - line 27; claims 1-18		
A	WO,A,93 14044 (UNIVERSITY OF CINCINNATI) 22 July 1993		12-81, 83-125, 137,138, 140
	see page 2, line 15 - page 7, line 14; claims 1-33		140
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PCT/US 95/06387

Box I	Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This in	ternational search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
1.	Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. X	Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
	Claims 1-8 missing upon filling, claims 9-11 are depending on these.
3.	Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Roy II	Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This Int	ernational Searching Authority found multiple inventions in this international application, as follows:
	See annex.
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2.	As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.	As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. X	No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
	12-81,83-125,137-138,140-142
Remark	on Protest
	No protest accompanied the payment of additional search fees.
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Form PCT/ISA/210 (continuation of first sheet (1)) (July 1992)

Internati nal Applicati n N . PCT/US95/06387

FURTHER INFORMATION CONTINUED FROM PCT/ISA/210

LACK OF UNITY OF INVENTION

1. Claims: 12-81, 83-125, 137, 138, 140

2. Claim: 82

3. Claims: 126-133

4. Claims: 134-136, 139

5. Claims: 143-145

information on patent family members

Into nal Application No PCT/US 95/06387

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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 US

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 12 December 1994 (12.12.94)
 US

 08/369,426
 6 January 1995 (06.01.95)
 US

 08/395,576
 28 February 1995 (28.02.95)
 US

 PCT/US95/04935
 21 April 1995 (21.04.95)
 WO

(34) Countries for which the regional or

international application was filed: US et al.

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(60) Parent Applications or Grants

(63) Related by Continuation

US 08/369,426 (CIP) Filed on 6 January 1995 (06.01.95) US 08/297,023 (CIP) Filed on 29 August 1994 (29.08.94) US 08/353,727 (CIP) 12 December 1994 (12.12.94) Filed on US 08/395,576 (CIP) Filed on 28 February 1995 (28.02.95) US PCT/US95/04935 (CIP) Filed on 21 April 1995 (21.04.95)

(71) Applicant (for all designated States except US): MICROPY-RETICS HEATERS INTERNATIONAL [US/US]; 1776 Mentor Avenue, Cincinnati, OH 45212 (US). (72) Inventors; and

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(74) Agents: DESHMUKH, Jayadeep, R. et al.; Dinsmore & Shohl, 1900 Chemed Center, 255 East Fifth Street, Cincinnati, OH 45202 (US).

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